

For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAENSIS





Digitized by the Internet Archive
in 2019 with funding from
University of Alberta Libraries

<https://archive.org/details/Lomnes1965>

THE UNIVERSITY OF ALBERTA
THE PHOTO-THERMOELECTRIC EFFECT IN
CADMIUM SULFIDE

BY

RANDY KEITH LOMNES

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF PHYSICS
EDMONTON, ALBERTA
OCTOBER 1965

UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled THE PHOTO-THERMOELECTRIC EFFECT IN CADMIUM SULFIDE, submitted by Randy Keith Lomnes in partial fulfilment of the requirements for the degree of Master of Science.

ACKNOWLEDGEMENTS

I wish to sincerely thank Dr. F.L. Weichman for suggesting this project and for his guidance in the major part of the research. It was unfortunate that Dr. Weichman was unable to be present for the completion of this work, consequently I am deeply indebted to Dr. S.B. Woods for his time and help in preparing the final draft of this thesis.

Further, to Mr. Peter Alexander and Mr. N. Riebeek I owe a special note of gratitude for their help in constructing various glass and metal components of the apparatus.

Finally I would like to express my appreciation for the financial assistance of the National Research Council.

ABSTRACT

The photo-thermoelectric effect is defined as the change that occurs in the thermoelectric voltage when a semiconductor is exposed to illumination. This effect was studied experimentally in commercially prepared samples of cadmium sulfide for the purpose of exploring its possibilities in studying semiconductors. The theory reveals the feasibility of experimentally finding information on the scattering of charge carriers and also of determining the ratio of the carrier mobilities. The experimental results on CdS using white light, indicate that the experiment must be performed to a high degree of accuracy before the above mentioned information can be extracted for a material where the mobility ratio is quite large. For this reason the information that could be obtained about CdS from the photo-thermoelectric effect using white light would probably be more easily obtained by other types of experiments. However the possibility is raised that this effect might yield some information on energy levels within the forbidden band by using light of different wavelengths to span the spectrum.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

ABSTRACT

CHAPTER ONE - INTRODUCTION 1

CHAPTER TWO - THEORY

Part A Fundamental equations 3

Part B Effect of light on semiconductors 7

Part C Generation of an emf 12

Application of the theory 25

CHAPTER THREE -

Experimental apparatus 28

CHAPTER FOUR

Experimental procedures 34

CHAPTER FIVE

Results of experiments 42

CHAPTER SIX

Discussion 57

CHAPTER SEVEN

Conclusions 60

BIBLIOGRAPHY 62

LIST OF FIGURES

1. Quasi-Fermi levels	9
2. Model circuit	13
3. Cross section of apparatus	29
4. Illuminated portion of the sample	30
5. Sample mounted in apparatus	30
6. Circuit diagram	31
7. Evaporator	37
8. Masked area of sample	37
9. Wetting apparatus	39
10. Resistance changes of sample after illumination	43
11. Resistance changes when illumination is stopped	44
12. Thermoelectric power of CdS	47
13. Photo-thermoelectric power for white light	49
14. Conductivity verses wavelength of illumination	54
15. Photo-thermoelectric power verses wavelength	55

LIST OF TABLES

1. Data for white light	46
2. Data for finding best straight line	46
3. Data for colored light	53

CHAPTER ONE

INTRODUCTION

This thesis is concerned with the generation of an electromotive force (emf) within the volume of a semiconductor. Generation of an emf requires an input of energy, of which two types (optical and thermal) will be considered here. If optical energy should cause an emf then the phenomena is termed the photovoltaic effect. If a temperature gradient across the semiconductor causes an emf to be set up then a thermoelectric effect is said to exist.

The composite effect, the change in the thermoelectric voltage that occurs when a semiconductor is illuminated, has been called the "photo-thermoelectric effect" by J. Tauc (1955a). It is this effect which is to constitute the subject of this manuscript.

The original paper on this subject was written by Tauc in 1955. Starting with some of the principles of irreversible thermodynamics he derived workable equations for the photo-thermoelectric effect and found that his theory agreed reasonably well with experiments performed on germanium. His experimental results showed that the photo-thermoelectric power was linear with $\Delta\sigma/\sigma_0$ when $\Delta\sigma/\sigma_0 \ll 1$ as expected by theory, where $\Delta\sigma$ is the change in the electrical conductivity due to illumination, and σ_0 is the conductivity in darkness. For germanium these experiments gave

$$\Delta\alpha = (120 \mu \text{ Volts/deg})(\Delta\sigma/\sigma_0)$$

where $\Delta\alpha$ is the photo-thermoelectric power and $\Delta\sigma/\sigma_0 < 0.1$.

The experimental study for this thesis was carried out on single crystals of high-resistivity cadmium sulfide. Since these samples were strongly photoconducting,

some changes had to be made to the equations derived by Tauc. These changes along with the complete derivation for the equations is given in chapter two. Much of the information used in this chapter was obtained from the book Photo and Thermoelectric Effects in Semiconductors by J. Tauc (pp. 72 - 173); however other sources which are listed in the bibliography proved very useful.

It appears from my survey of the literature that very little work has been done on the photo-thermoelectric effect. For this reason the present work has been undertaken with two objectives in mind:

- 1) To see if useful information about semiconductor parameters can be obtained from measurements of the photo-thermoelectric effect.
- 2) To see what the photo-thermoelectric effect can tell us about the properties of cadmium sulfide.

CHAPTER TWO

THEORY - PART A

As a starting point the following theorem from irreversible thermodynamics is used.

If one can express the creation of entropy per second by an equation of the form,

$$\frac{d}{dt} dS = \sum_i (\vec{J}_i \cdot \vec{X}_i) \quad ,$$

where \vec{J}_i are quantities defined as generalized forces satisfying the expression,

$$\vec{J}_i = \sum_j a_{ij} \vec{X}_j$$

then Onsagers theorem gives the result,

$$a_{ij} = a_{ji} \quad .$$

With this theorem in mind consider a system which can be described by two currents;

- 1) a particle current density \vec{J}_N ,
and 2) a thermal current density \vec{J}_q .

The problem then is to find the conjugate forces \vec{X}_N and \vec{X}_q and the coefficients a_{ij} .

If the electrons in the conduction band of a semiconductor are the system under consideration, then \vec{J}_N becomes \vec{J}_{nN} , the particle current of the electrons and \vec{J}_q becomes \vec{J}_{nq} , the heat current in the electron system.

When the number of particles n can vary and the volume is constant, the following thermodynamic relation can be used

$$T ds_n = du_n - \zeta'_n dn$$

where s_n is the entropy per unit volume, u_n is the

energy per unit volume and ζ'_n is the chemical potential of the assembly of electrons. The above equation can also be written as

$$T \frac{\partial s_n}{\partial t} = \frac{\partial u_n}{\partial t} - \zeta'_n \frac{\partial n}{\partial t} \quad (1)$$

where t is the time.

The continuity equation for the particle current can be written as

$$\nabla \cdot \vec{J}_{nN} = \frac{\partial n}{\partial t} \quad (2)$$

Also a balance equation for the internal energy gives

$$\frac{\partial u_n}{\partial t} = \nabla \cdot \vec{J}_{nq} - e \vec{J}_{nN} \cdot \nabla \phi \quad (3)$$

where ϕ is the electric potential existing in the system.

Substituting equations (2) and (3) into (1) gives

$$\frac{\partial s_n}{\partial t} = \frac{1}{T} \nabla \cdot \vec{J}_{nq} - \frac{e}{T} \vec{J}_{nN} \cdot \nabla \phi - \frac{\zeta'_n}{T} \nabla \cdot \vec{J}_{nN} \quad .$$

One can write the identities

$$\frac{\zeta'_n}{T} \nabla \cdot \vec{J}_{nN} = \nabla \cdot \left\{ \frac{\zeta'_n}{T} \vec{J}_{nN} \right\} - \vec{J}_{nN} \cdot \nabla \left\{ \frac{\zeta'_n}{T} \right\}$$

and

$$\frac{1}{T} \nabla \cdot \vec{J}_{nq} = \nabla \cdot \left\{ \frac{\vec{J}_{nq}}{T} \right\} - \vec{J}_{nq} \cdot \nabla \left\{ \frac{1}{T} \right\} \quad .$$

Hence

$$\frac{\partial s_n}{\partial t} = \nabla \cdot \left\{ \frac{\vec{J}_{nq} - \zeta'_n \vec{J}_{nN}}{T} \right\} + \frac{1}{T} \vec{J}_{nq} \cdot \nabla T - \frac{e}{T} \vec{J}_{nN} \cdot \nabla \phi + \vec{J}_{nN} \cdot \nabla \left\{ \frac{\zeta'_n}{T} \right\} \quad . \quad (4)$$

Define the entropy current as

$$\vec{J}_{ns} = \left\{ \frac{\vec{J}_{nq} - \zeta'_n \vec{J}_{nN}}{T} \right\} \quad ,$$

then equation (4) becomes

$$\frac{\partial s_n}{\partial t} - \nabla \cdot \vec{J}_{ns} = \frac{1}{T} \left\{ \vec{J}_{nN} \cdot \left[-e \nabla \phi + T \nabla \left(\frac{\zeta'_n}{T} \right) \right] + \frac{1}{T} \vec{J}_{nq} \cdot \nabla T \right\} \quad (5) \quad .$$

Equation (5) is in the form of a continuity equation for the entropy. The term $\partial s_n / \partial t$ represents the total rate of change of entropy in some volume V , the term $\nabla \cdot \vec{J}_{ns}$ represents the flow of entropy across the surface of volume V and the final term on the right hand side represents the creation of entropy in the volume V .

Hence an expression for the creation of entropy has been derived which is in the form

$$\frac{\partial}{\partial t} dS = \sum_i \vec{J}_i \cdot \vec{X}_i$$

The two conjugate forces are easily seen to be

$$\vec{X}_{nN} = -e\nabla\phi + T\nabla(\xi'_n / T)$$

and

$$\vec{X}_{nq} = \frac{1}{T} \nabla T .$$

Onsager's theorem can be applied to give $a_{ij} = a_{ji}$ in the following equations;

$$\vec{J}_{nN} = a_{11} \{ -e\nabla\phi + T \nabla(\xi'_n / T) \} + a_{12} \frac{1}{T} \nabla T \quad (6)$$

$$\vec{J}_{nq} = a_{21} \{ -e\nabla\phi + T \nabla(\xi'_n / T) \} + a_{22} \frac{1}{T} \nabla T . \quad (7)$$

The coefficients a_{ij} can be evaluated in the following way. Consider the case of constant chemical potential and zero temperature gradient, then Ohm's law can be used to give a_{11} .

$$\vec{J}_n = -e\vec{J}_{nN} = -\sigma_n \nabla\phi$$

from which

$$a_{11} = -\sigma_n / e^2$$

where \vec{J}_n is the electron current density.

Similarly Fourier's law of thermal conduction gives

$$a_{22} = -\kappa_n T .$$

The third coefficient a_{21} can be evaluated by setting $\nabla T = 0$ and dividing equation (6) by (7), then

$$(|\vec{J}_{nq}| / |\vec{J}_{nN}|) = a_{21}/a_{11} \quad .$$

Define $Q'_n = |\vec{J}_{nq}| / |\vec{J}_{nN}|$.

The quantity Q'_n is called the "heat of electron transfer" and can be considered as the thermal current density transferred by one electron $\text{cm}^{-2} \text{sec}^{-1}$. The significance of Q'_n will be discussed in more detail in part C of the theory.

The current density due to the electrons can now be written as

$$\vec{J}_n = -e\vec{J}_{nN} = \frac{\sigma_n}{e} \{ -e\nabla\phi + T \nabla(\xi'_n/T) + (Q'_n/T) \nabla T \}.$$

If the holes in the valence band are considered then an identical expression for the hole current density can be obtained:

$$\vec{J}_p = \frac{\sigma_p}{e} \{ -e\nabla\phi + T \nabla(\xi'_p/T) + (Q'_p/T) \nabla T \}.$$

The above equations can be reduced once more by expanding $\nabla(\xi'_n/T)$ and $\nabla(\xi'_p/T)$.

Thus

$$\vec{J}_n = \frac{\sigma_n}{e} \{ -e\nabla\phi + \nabla\xi'_n + \left[\frac{Q'_n - \xi'_p}{T} \right] \nabla T \} \quad (8)$$

and

$$\vec{J}_p = \frac{\sigma_p}{e} \{ -e\nabla\phi + \nabla\xi'_p + \left[\frac{Q'_p - \xi'_p}{T} \right] \nabla T \} \quad (9)$$

THEORY - PART B

The absorption of light by a solid is a quantum process in which electrons are raised from lower into higher levels. In a semiconductor, if the energy of the light quanta is sufficient, electrons from the valence band can be given ample energy to cross the energy gap into the conduction band, and when this happens both the free electron and hole densities are increased.

When electrons are first raised into the conduction band the resulting carriers may have considerably more energy than the carriers resulting from thermal excitations. Because a strong interaction exists between the electrons and lattice, the electrons will lose their excess energy and sink to the bottom of the conduction band in times of about 10^{-10} to 10^{-11} sec. Since the average lifetime of an electron in the conduction band is usually longer than 10^{-6} sec., these optically excited carriers spend the major portion of their lifetimes at energies approximately the same as that for electrons present from thermal excitation. It is therefore assumed to a first approximation that all the electrons in the conduction band and all the holes in the valence band can be associated with a temperature T (i.e. with the temperature of the lattice). The energy absorbed by the lattice from the optically excited carriers is assumed to cause only a negligible change in T which can be ignored to a first approximation.

It is reasonable to expect that the electrons and holes will be described by a distribution function, which will necessarily be the Fermi-Dirac distribution function. Optical excitation will increase both the electron and hole concentrations, however looking at the distribution function

$$f(E) = \frac{1}{1 + \exp((E - \xi'_0)/kT)} ,$$

(where ζ'_0 is the Fermi level), it is seen that the only way it can describe an increase in both types of carrier densities is for the temperature T to rise (see figure 1a). However it has been assumed that temperature changes due to absorbed light are negligible. In order to increase both types of carrier densities without requiring a temperature change, the common practice is to shift the Fermi level to the right to increase the electron concentrations and shift the Fermi level to the left to raise the hole concentrations, (see figure 1b). Thus two distribution functions are used, one for the electrons and one for the holes, with different Fermi levels. Then the electron concentration in the conduction band is given by

$$n = \int_{E_c}^{\infty} \frac{Z(E) dE}{1 + \exp((E - \zeta'_n)/kT)}$$

$$p = \int_{-\infty}^{E_v} Z(E) \left\{ 1 - \frac{1}{1 + \exp((E - \zeta'_p)/kT)} \right\} dE$$

where $Z(E)$ is the density of states available for the electrons and holes, and ζ'_n and ζ'_p are known as the quasi-Fermi levels or the chemical potentials of the electron and hole assemblies.

When optically excited carriers are not present $\zeta'_n \rightarrow \zeta'_{n0}$, $\zeta'_p \rightarrow \zeta'_{p0}$, and $\zeta'_{n0} = \zeta'_{p0} = \zeta'_0$ = the Fermi level. The index $_0$ refers to the non-illuminated condition.

Take E_v to be the zero of energy and introduce

$$\epsilon_n = E - E_g = \text{kinetic energy of the electrons,}$$

$$\epsilon_p = -E = \text{kinetic energy of the holes,}$$

$$\zeta_n = \zeta'_n - E_g$$

and $\zeta_p = -\zeta'_p$, where E_v is the energy at the top of valence band.

The densities of electrons and holes in the conduction and valence bands respectively are then given by

FIGURE 1 (a & b)

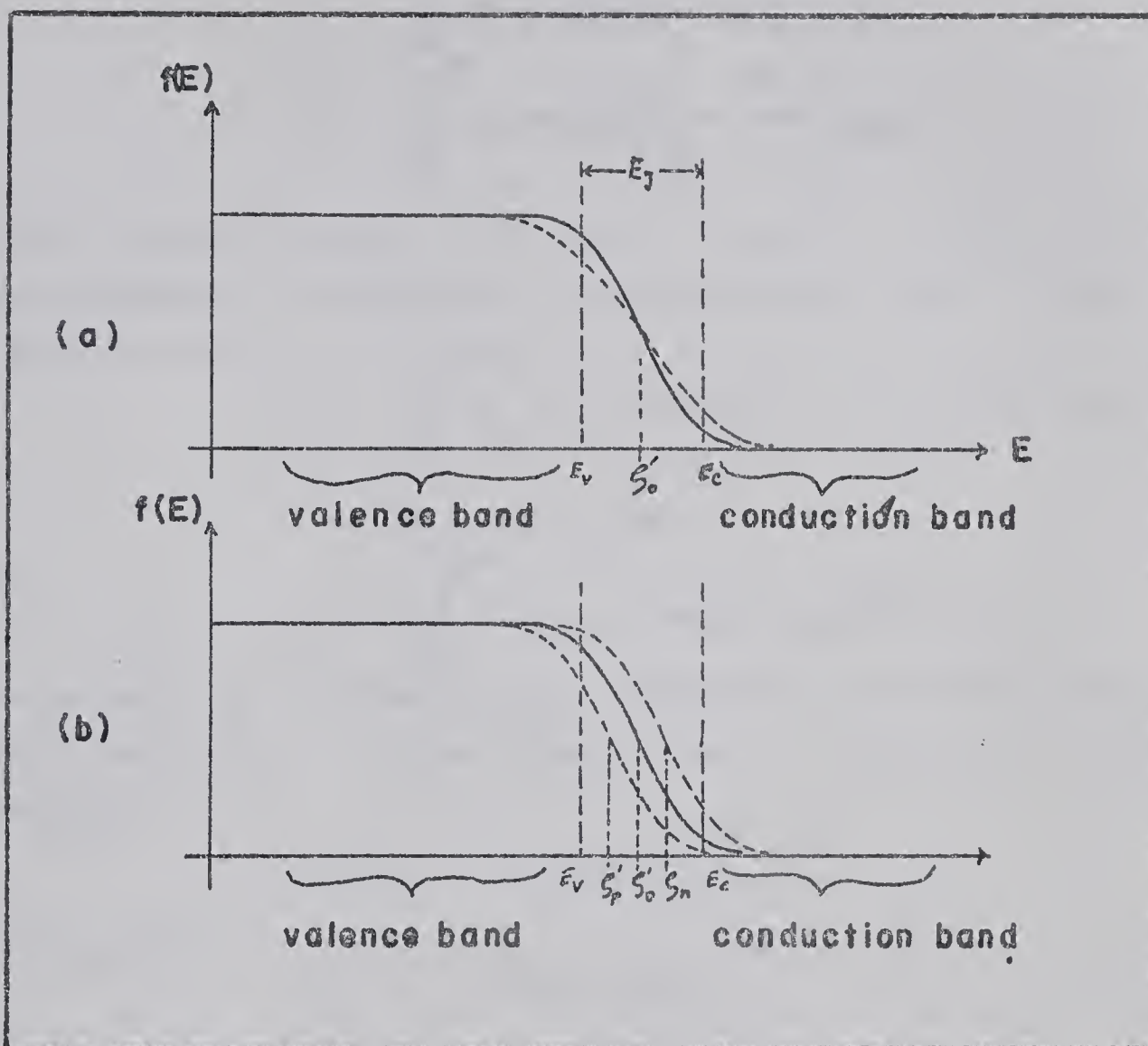
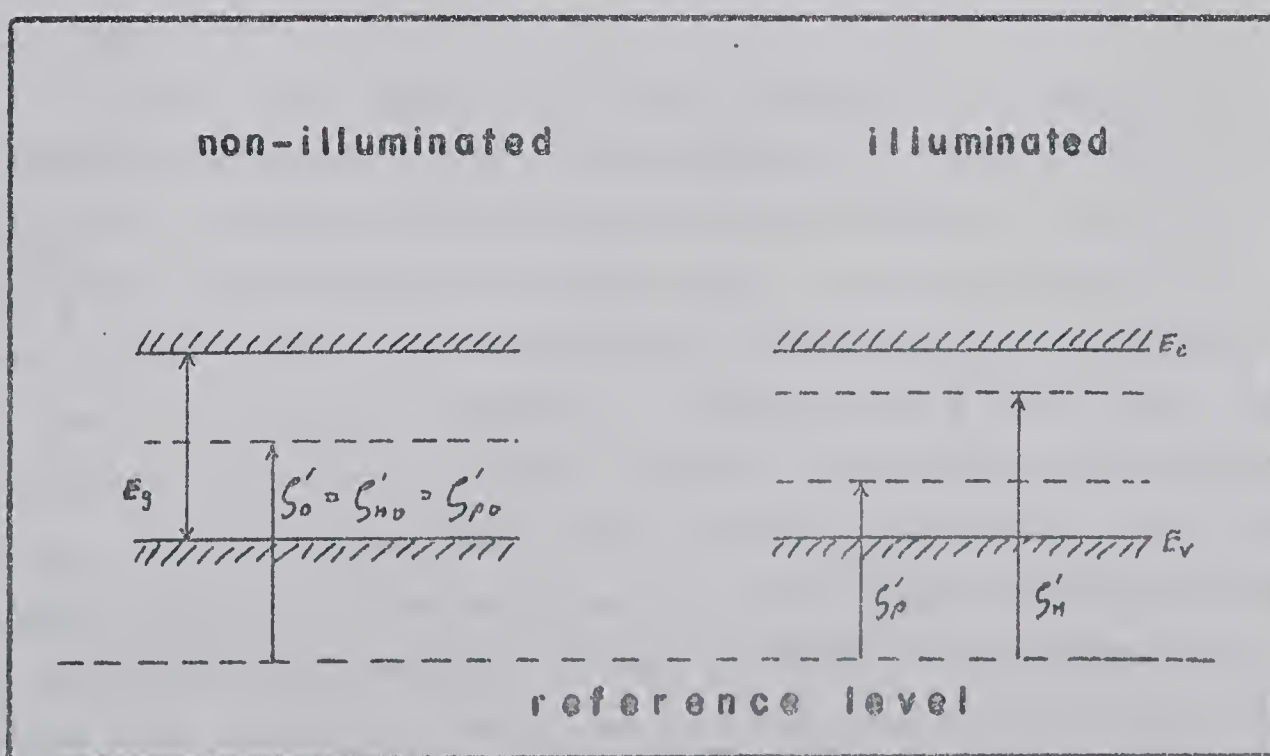


FIGURE 1 (c)



$$n = \int_0^{\infty} \frac{Z_n(\epsilon_n) d\epsilon_n}{1 + \exp(\epsilon_n - \zeta_n)/kT}$$

$$p = \int_0^{\infty} \frac{Z_p(\epsilon_p) d\epsilon_p}{1 + \exp(\epsilon_p - \zeta_p)/kT}$$

If the conditions are such that $-\zeta_n/kT > 4$ and $-\zeta_p/kT > 4$ then classical statistics can be employed with less than 2% error and

$$n = \int_0^{\infty} Z_n(\epsilon_n) \exp(-(\epsilon_n - \zeta_n)/kT) d\epsilon_n$$

$$= N_c \exp(\zeta_n/kT)$$

where

$$N_c = \int_0^{\infty} Z_n(\epsilon_n) \exp(-\epsilon_n/kT) d\epsilon_n$$

The density of states $Z_n(\epsilon_n)$ depends on the Brillouin zone structure. In the simple case of spherical energy surfaces

$$Z_n(\epsilon_n) = 4\pi(2m_n^*/h^2)^{3/2} \epsilon_n^{1/2}$$

which gives

$$N_c = 2(2\pi m_n^* kT/h^2)^{3/2}$$

where m_n^* is the effective mass of the electron.

Derivations of these equations can be found in references (2) and (5).

Free electrons and holes generated solely by thermal excitation will be defined as equilibrium carriers. This definition is used because the densities of ^{these} free electrons and holes are in equilibrium with each other, that is to say the internal heat reservoir of the lattice is capable of maintaining the hole and electron densities. When excess carriers are generated (e.g., by illumination) the lattice vibrations can no longer maintain the excess hole and electron densities. If the external source of excitation ceases, the free holes and electrons will recombine and their densities will reduce back to the densities that the lattice vibrations can maintain. For this reason carriers

excited by means other than thermal ionization will be defined as non-equilibrium carriers.

By the assumption that the lattice temperature does not increase when a semiconductor is illuminated, it is possible to say that any variation in the excitation will change only the density of the non-equilibrium carriers without affecting the density of the equilibrium ones, thus the total density is simply the sum of the equilibrium and the non-equilibrium carriers. Therefore one can write

$$\begin{aligned} n &= n_o + \Delta n \\ \text{and} \quad p &= p_o + \Delta p \end{aligned}$$

where Δn and Δp are the non-equilibrium densities and n_o and p_o are the equilibrium densities. Hence the conductivity can be written

$$\begin{aligned} \sigma &= e(n\mu_n + p\mu_p) = \sigma_n + \sigma_p \\ &= e(n_o\mu_n + p_o\mu_p) + e(\Delta n\mu_n + \Delta p\mu_p) \\ &= \sigma_o + \Delta\sigma, \text{ where } \mu_n \text{ and } \mu_p \text{ are the mobilities.} \end{aligned}$$

In the above equation it is assumed that non-equilibrium and equilibrium carriers have the same mobilities. This assumption is reasonable since the non-equilibrium and equilibrium carriers are both taken to have the same temperature and mobility is a function of temperature.

THEORY - PART C

Consider the hypothetical model shown in figure (2). By using this model any complicated junction phenomena can^{be}/avoided. The entire temperature drop takes place inside the illuminated portion. The points a and a' are chosen to have identical chemical composition and to be at the same temperature. Points b and g are taken to be sufficiently far from the illuminated part so that in their neighborhood, the non-equilibrium concentrations of current carriers are zero. Furthermore Δn is assumed to be constant across the region of temperature change, all the changes in Δn taking place in the neighborhood of points c and f.

In addition to the above, the geometry is taken to be linear. In practice this last consideration means that the thickness of the sample must be small compared with the reciprocal of the absorption coefficient, or with the diffusion length of the carriers, so that the concentrations are practically constant over the whole cross-section of the sample.

The potential between points a and a' will be given by an expression of the form

$$U = - \int_a^{a'} \frac{d\phi}{dx} dx \quad .$$

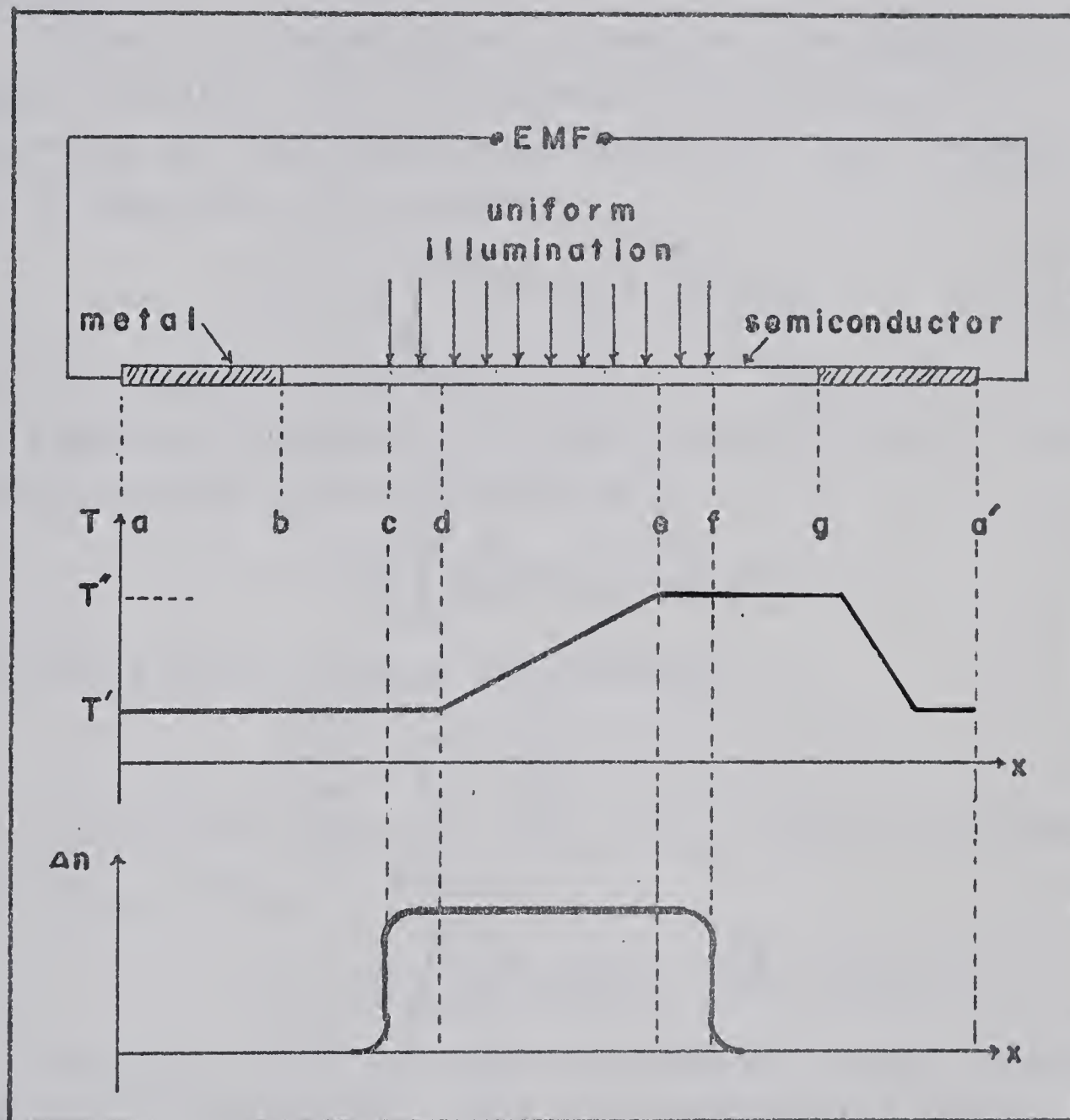
To evaluate the emf U, use is made of equations (8) and (9) of part A. The total current density \vec{J} is given by $\vec{J}_n + \vec{J}_p$ and since it is the open circuit emf that is of interest, $\vec{J} = 0$. Putting $\vec{J}_n + \vec{J}_p = 0$ one can solve for $d\phi/dx$. One obtains

$$\frac{d\phi}{dx} = \frac{1}{e} \left\{ \frac{\sigma_n}{\sigma} \frac{d\zeta_n'}{dx} + \frac{\sigma_p}{\sigma} \frac{d\zeta_p'}{dx} \right\} + \frac{k}{e} \left\{ \frac{\sigma_n}{\sigma} \left[\frac{Q_n' - \zeta_n'}{kT} \right] + \frac{\sigma_p}{\sigma} \left[\frac{Q_p - \zeta_p'}{kT} \right] \right\} \frac{dT}{dx} \quad .$$

The potential between points a and a' is therefore given by

$$U = - \frac{1}{e} \int_a^{a'} \left\{ \frac{\sigma_n}{\sigma} d\zeta_n' + \frac{\sigma_p}{\sigma} d\zeta_p' \right\} - \frac{k}{e} \int_a^{a'} \left\{ \frac{\sigma_n}{\sigma} \left[\frac{Q_n' - \zeta_n'}{kT} \right] + \frac{\sigma_p}{\sigma} \left[\frac{Q_p - \zeta_p'}{kT} \right] \right\} dT \quad (11) \quad .$$

FIGURE 2



MODEL CIRCUIT

This last equation describes the conditions by which an emf can be generated in a semiconductor. Three separate cases will now be discussed.

Case 1:

When the temperature is constant throughout the sample, equation (11) will yield the expression governing the bulk photovoltaic effect. That is when $dT = 0$ equation (11) becomes

$$U = - \frac{1}{e} \int_a^{a'} \left[\frac{\sigma_n}{\sigma} d\zeta'_n + \frac{\sigma_p}{\sigma} d\zeta'_p \right] .$$

With the change of variables $\zeta_n = \zeta'_n - E_g$ and $\zeta_p = \zeta'_p$ and assuming that $\text{grad } E_g$ is zero along the sample, the bulk photovoltaic emf is given by

$$U = - \frac{1}{e} \int_a^{a'} \left[\frac{\sigma_n}{\sigma} d\zeta_n + \frac{\sigma_p}{\sigma} d\zeta_p \right] .$$

Make the further changes of variable

$$\Delta\zeta_n = \zeta_n - \zeta_{no}$$

$$\Delta\zeta_p = \zeta_p - \zeta_{po}$$

and use the fact that $\zeta_{no} + \zeta_{po} = E_g$, then it follows that $d\zeta_{no} = -d\zeta_{po}$. Finally

$$U = - \frac{1}{e} \int_a^{a'} \left[\frac{\sigma_n}{\sigma} d(\Delta\zeta_n) - \frac{\sigma_p}{\sigma} d(\Delta\zeta_p) \right] . \quad (12)$$

Equation (12) provides information on the conditions required for generation of a bulk photovoltaic emf.

- a) If the sample is in darkness, i.e. the non-equilibrium concentrations are zero, then $\Delta\zeta_n = \Delta\zeta_p = 0$ and $U = 0$.
- b) The integral for U is always equal to zero if there is only one kind of current carrier present (i.e. $\sigma_p / \sigma = 0$ and $\sigma_n / \sigma = 1$, or $\sigma_p / \sigma = 1$ and $\sigma_n / \sigma = 0$).
- c) U may still be zero even when the sample is illuminated if the semiconductor is homogeneous in darkness. Homogeneous in darkness can be taken to mean that (μ_n / μ_p)

is constant along the length of the sample. In this case (σ_n / σ) , (σ_p / σ) , $\Delta\zeta_n$, and $\Delta\zeta_p$ merely become functions of Δn and integration between the identical points a and a' becomes zero.

The condition for the generation of a bulk photovoltaic emf is therefore the simultaneous presence of non-equilibrium concentrations and of an inhomogeneity, as the integral in equation (12) differs from zero only if (σ_n / σ) , (σ_p / σ) , $\Delta\zeta_n$, and $\Delta\zeta_p$ vary along the sample in such a way that they cannot be expressed as single valued functions of one variable. Consequently the presence of at least two independent factors determining (σ_n / σ) , (σ_p / σ) , $\Delta\zeta_n$, and $\Delta\zeta_p$ is necessary. For example a second factor could be a variation in donor or acceptor concentrations along the sample.

Case 2:

When a sample with a temperature gradient does not contain non-equilibrium carriers, equation (11) will yield the expression governing the thermoelectric effect. The first integral of equation (11) can be put equal to zero, leaving

$$U = - \frac{k}{e} \int \left\{ \frac{\sigma_{no}}{\sigma_o} \left[\frac{Q'_{no} - \zeta'_{no}}{kT} \right] + \frac{\sigma_{po}}{\sigma_o} \left[\frac{Q'_{po} - \zeta'_{po}}{kT} \right] \right\} dT$$

where the index o refers to the non-illuminated state. Use substitutions (10) and the thermoelectric emf becomes

$$U = - \frac{k}{e} \int \left\{ \frac{\sigma_{no}}{\sigma_o} \left[\frac{Q_{no} - \zeta_{no}}{kT} \right] + \frac{\sigma_{po}}{\sigma_o} \left[\frac{Q_{po} - \zeta_{po}}{kT} \right] \right\} dT. \quad (13)$$

Define the thermoelectric power by the expression

$$\alpha = \lim_{\Delta T \rightarrow 0} \left\{ \frac{U}{\Delta T} \right\}.$$

Equation (13) then gives for the thermoelectric power

$$\alpha = \frac{k}{e} \left\{ \frac{\sigma_{no}}{\sigma_o} \left[\frac{\zeta_{no} - Q_{no}}{kT} \right] - \frac{\sigma_{po}}{\sigma_o} \left[\frac{\zeta_{po} - Q_{po}}{kT} \right] \right\}.$$

Furthermore define the thermoelectric power for electrons by

$$\alpha_n = \frac{k}{e} \left[\frac{\zeta_{no} - Q_{no}}{kT} \right]$$

and the thermoelectric power for holes by

$$\alpha_p = \frac{k}{e} \left[\frac{\zeta_{po} - Q_{po}}{kT} \right]$$

Then

$$\alpha = \frac{\sigma_{no}}{\sigma_o} \alpha_n - \frac{\sigma_{po}}{\sigma_o} \alpha_p \quad .$$

From the definition of U it is seen that $U < 0$ when the cold side is negative and $U > 0$ when the cold side is positive. Since α_n and α_p are both negative if the Fermi level is inside the forbidden band, it is evident that $\alpha < 0$ when the semiconductor is n type or the ratio of the mobilities μ_n / μ_p is very large. Thus

$$\alpha = \alpha_n = \frac{k}{e} \left[\frac{\zeta_{no} - Q_{no}}{kT} \right] \quad . \quad (14)$$

A knowledge of Q_{no} will therefore enable one to calculate the Fermi level ζ_{no} from measurements of the thermoelectric power.

Case 3: The Photo-thermoelectric Emf

When a temperature gradient exists across the sample, the presence of non-equilibrium carrier concentrations causes a change in the thermoelectric voltage, the calculation of this emf will require the use of both parts of equation (11). The assumptions outlined below will be made in the calculations to follow.

- a) Classical statistics are assumed to hold.
- b) Changes in Δn occur only in regions of constant temperature, (see figure 2).
- c) Any deviation from intrinsic conductivity is assumed to result from a net concentration $|N|$ of impurities, where $N < 0$ for donor impurities and $N > 0$ for acceptor impurities. It is further assumed that in the

temperature region of interest ($T > 300^\circ\text{K}$) that all impurity states are ionized. This enables one to write $n_o = N + p_o$.

- d) The semiconductor is assumed to be homogeneous, i.e. $dN/dx = 0$. This implies that $dn_o = dp_o$.
- e) Since the impurity states are assumed to be completely ionized the relationship $\Delta p = \Delta n$ must hold for the non-equilibrium carriers, because every electron excited to the conduction band by illumination must come from the valence band and leave a hole.
- f) The energy surfaces are spherical so that
$$N_c = 2(2\pi m_n^* kT/h^2)^{3/2} .$$
- g) The temperature gradient is small compared with the average temperature of the sample.

Now use substitutions (10) in equation (11) to get

$$U = -\frac{1}{e} \int \left[\frac{\sigma_n}{\sigma} d\zeta_n - \frac{\sigma_p}{\sigma} d\zeta_p \right] - \frac{k}{e} \int \left\{ \frac{\sigma_n}{\sigma} \left[\frac{Q_n - \zeta_n}{kT} - \frac{1}{k} \frac{dE_g}{dT} \right] - \frac{\sigma_p}{\sigma} \left[\frac{Q_p - \zeta_p}{kT} \right] \right\} dT \quad (15)$$

Classical statistics provide the equation

$n = N_c \exp(\zeta_n / kT)$, where $N_c = 2(2\pi m_n^* kT/h^2)^{3/2}$ from which it is easily shown that

$$d\zeta_n = \frac{\partial \zeta_n}{\partial T} dT + \frac{\partial \zeta_n}{\partial n} dn = k \left[\frac{\zeta_n}{kT} - \frac{3}{2} \right] dT + kT \frac{dn}{n} .$$

Similarly for holes

$$d\zeta_p = k \left[\frac{\zeta_p}{kT} - \frac{3}{2} \right] dT + kT \frac{dp}{p} .$$

With the above substitutions equation (15) becomes

$$U = -\frac{k}{e} \int \left\{ \frac{\sigma_n}{\sigma} \left[\frac{Q_n}{kT} - \frac{3}{2} - \frac{1}{k} \frac{dE_g}{dT} \right] - \frac{\sigma_p}{\sigma} \left[\frac{Q_p}{kT} - \frac{3}{2} \right] \right\} dT - \frac{k}{e} \int T \left[\frac{\sigma_n}{\sigma} \frac{dn}{n} - \frac{\sigma_p}{\sigma} \frac{dp}{p} \right] . \quad (16)$$

The integrals in the above expression can be

evaluated by dealing with each region in figure (2) separately.

- 1) In the metal region (a,b), $dT = dn = dp = 0$ and the contribution to U is zero.
- 2) In the metal region (g,a'), $dT \neq 0$. The contribution from this region is just the non-illuminated thermoelectric effect of the metal between temperature T' and T'' . Since metal thermoelectric powers are usually more than an order of magnitude smaller than semiconductor thermoelectric powers, the contribution to U can be ignored.
- 3) In the semiconductor region (b,c), $dn = dp = 0$ and the contribution to U is zero.
- 4) Region (f,g) is the same as (b,c) and gives zero contribution.
- 5) In the region (c,d), $dT = 0$ but $dn \neq 0$ and $dp \neq 0$. To evaluate the contribution of this region use

$$n = n_o + \Delta n$$

$$\text{and } p = p_o + \Delta p$$

$$\text{which give } dn = d(\Delta n)$$

$$\text{and } dp = d(\Delta p)$$

because the temperature is assumed to be constant in this region. Also by assumption (e),

$$d(\Delta n) = d(\Delta p) .$$

Thus the contribution to U becomes

$$\begin{aligned} -T' \frac{k}{e} \int_c^d \left\{ \frac{\sigma_n}{\sigma} \frac{d(\Delta n)}{n} - \frac{\sigma_p}{\sigma} \frac{d(\Delta p)}{p} \right\} &= -T' \frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \int_0^{\Delta \sigma} \frac{d(\Delta \sigma)}{\sigma_o' + \sigma \Delta} \\ &= - \frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] T' \ln(1 + \Delta \sigma / \sigma_o') \end{aligned}$$

where σ_o' refers to the dark conductivity at temperature T' .

- 6) The region (e,f) is exactly the same as region (c,d) except for a change in sign and temperature, thus the

contribution is

$$+ \frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] T'' \ln(1 + \Delta\sigma/\sigma''_0) .$$

7) In the region (d,e), $dT \neq 0$, $dn \neq 0$ and $dp \neq 0$.

The equations $n = n_0 + \Delta n$

$$p = p_0 + \Delta p$$

give $dn = dn_0$ and $dp = dp_0$ because Δn and Δp are assumed to be constant in (d,e). Also by assumption (d), $dn_0 = dp_0$.

Hence the contribution to U from (d,e) is

$$- \frac{k}{e} \int \left\{ \frac{\sigma_n}{\sigma} \left[\frac{Q_n}{kT} - \frac{3}{2} - \frac{1}{k} \frac{dE_g}{dT} \right] - \frac{\sigma_p}{\sigma} \left[\frac{Q_p}{kT} - \frac{3}{2} \right] + \frac{T}{\sigma} \left[\frac{\sigma_n}{n} - \frac{\sigma_p}{p} \right] \frac{dn_0}{dT} \right\} dT \quad (17)$$

Collecting the contributions to U from all the regions gives the total emf between points a and a' ,

$$U = - \frac{k}{e} \int \left\{ \frac{\sigma_n}{\sigma} \left[\frac{Q_n}{kT} - \frac{3}{2} - \frac{1}{k} \frac{dE_g}{dT} \right] - \frac{\sigma_p}{\sigma} \left[\frac{Q_p}{kT} - \frac{3}{2} \right] + \frac{T}{\sigma} \left[\frac{\sigma_n}{n} - \frac{\sigma_p}{p} \right] \frac{dn_0}{dT} \right\} dT \\ - \frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \left[T' \ln(1 + \Delta\sigma/\sigma'_0) - T'' \ln(1 + \Delta\sigma/\sigma''_0) \right] . \quad (18)$$

The change that occurs with illumination of the sample is the quantity of interest. To get this, one must subtract the non-illuminated thermoelectric voltage U_0 from U . U_0 is simply obtained from expression (17) by placing the subscript 0 on the proper symbols.

$$U_0 = - \frac{k}{e} \int \left\{ \frac{\sigma_{n0}}{\sigma_0} \left[\frac{Q_{n0}}{kT} - \frac{3}{2} - \frac{1}{k} \frac{dE_g}{dT} \right] - \frac{\sigma_{p0}}{\sigma_0} \left[\frac{Q_{p0}}{kT} - \frac{3}{2} \right] + \frac{T}{\sigma_0} \left[\frac{\sigma_{n0}}{n_0} - \frac{\sigma_{p0}}{p_0} \right] \frac{dn_0}{dT} \right\} dT .$$

On page (23) the following expression is given for Q_n

$$Q_n = \frac{\int \tau_n \epsilon_n^2 Z_n(\epsilon_n) (\partial f_{n0} / \partial \epsilon_n) d\epsilon_n}{\int \tau_n \epsilon_n Z_n(\epsilon_n) (\partial f_{n0} / \partial \epsilon_n) d\epsilon_n}$$

so that for classical statistics it is possible to write $Q_{no} = Q_n$ in the equation for U_o . Thus the photo-thermoelectric voltage ΔU is given by

$$\begin{aligned}\Delta U &= U - U_o \\ &= -\frac{k}{e} \int \left\{ \left[\frac{Q_n}{kT} - \frac{3}{2} - \frac{1}{k} \frac{dE_g}{dT} \right] \left[\frac{\sigma_n}{\sigma} - \frac{\sigma_{no}}{\sigma_o} \right] - \left[\frac{Q_p}{kT} - \frac{3}{2} \right] \left[\frac{\sigma_p}{\sigma} - \frac{\sigma_{po}}{\sigma_o} \right] \right. \\ &\quad \left. + T \left\{ \left[\frac{\sigma_n}{n} - \frac{\sigma_p}{p} \right] \frac{1}{\sigma} - \left[\frac{\sigma_{no}}{n_o} - \frac{\sigma_{po}}{p_o} \right] \frac{1}{\sigma_o} \right\} \frac{dn_o}{dT} \right\} dT \\ &\quad - \frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \left[T' \ln(1 + \Delta\sigma/\sigma_o') - T'' \ln(1 + \Delta\sigma/\sigma_o'') \right].\end{aligned}$$

It is easily shown that

$$\left[\frac{\sigma_n}{\sigma} - \frac{\sigma_{no}}{\sigma_o} \right] = - \left[\frac{\sigma_p}{\sigma} - \frac{\sigma_{po}}{\sigma_o} \right],$$

thus

$$\begin{aligned}\Delta U &= -\frac{k}{e} \int \left\{ \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \left[\frac{\sigma_n}{\sigma} - \frac{\sigma_{no}}{\sigma_o} \right] \right. \\ &\quad \left. + eT [\mu_n - \mu_p] \left[\frac{1}{\sigma} - \frac{1}{\sigma_o} \right] \frac{dn_o}{dT} \right\} dT \\ &\quad - \frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \left[T' \ln(1 + \Delta\sigma/\sigma_o') - T'' \ln(1 + \Delta\sigma/\sigma_o'') \right].\end{aligned}\tag{19}$$

The temperature difference is assumed to be small, that is $T'' = T' + \Delta T$ where $\Delta T \ll T'$. The integral in equation (19) then becomes

$$-\frac{k}{e} \left\{ \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \left[\frac{\sigma_n}{\sigma} - \frac{\sigma_{no}}{\sigma_o} \right] + e[\mu_n - \mu_p] \left[\frac{1}{\sigma} - \frac{1}{\sigma_o} \right] T \frac{dn_o}{dT} \right\} \Delta T\tag{20}$$

To simplify the above, factor out $\Delta\sigma/\sigma$ and use the relation

$$\begin{aligned}\left[\frac{\sigma_n}{\sigma} - \frac{\sigma_{no}}{\sigma_o} \right] \left[\frac{\sigma}{\Delta\sigma} \right] &= \frac{(p_o - n_o) \mu_n \mu_p}{(\mu_n + \mu_p)(n_o \mu_n + p_o \mu_p)} \\ &= \frac{-N \mu_n \mu_p}{(\mu_n + \mu_p)(n_o \mu_n + p_o \mu_p)}\end{aligned}$$

and also

$$e(\mu_n - \mu_p) \left[\frac{1}{\sigma} - \frac{1}{\sigma_0} \right] \left[\frac{\sigma}{\Delta\sigma} \right] T \frac{dn_0}{dT} = - \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \frac{T}{\sigma_0} \frac{d\sigma_0}{dT} .$$

Expression (20) can then be written as

$$\frac{k}{e} \left\{ \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \left[\frac{N \mu_n \mu_p}{(\mu_n + \mu_p)(n_0 \mu_n + p_0 \mu_p)} \right] + \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \frac{T}{\sigma_0} \frac{d\sigma_0}{dT} \frac{\Delta\sigma}{\sigma} \right\} \Delta T .$$

Expand $\sigma'' = \sigma_0(T' + \Delta T)$ in a Taylor series, and for $\Delta T \ll T'$ one obtains the result $\sigma'' - \sigma'_0 \cong \frac{d\sigma_0}{dT} \Delta T$ where $|\sigma'' - \sigma'_0| \ll \sigma_0$.

Thus the remainder of equation (18) can be simplified as follows. First

$$\begin{aligned} & - \frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \left[T' \ln(1 + \Delta\sigma/\sigma'_0) - T'' \ln(1 + \Delta\sigma/\sigma''_0) \right] \\ & = \frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \left[\ln(1 + \Delta\sigma/\sigma'_0) - \frac{T''}{\Delta T} \ln \frac{(1 + \Delta\sigma/\sigma'_0)}{(1 + \Delta\sigma/\sigma''_0)} \right] \Delta T . \end{aligned} \quad (21)$$

Now consider the term

$$\ln \frac{(1 + \Delta\sigma/\sigma'_0)}{(1 + \Delta\sigma/\sigma''_0)} = \ln(\sigma''_0/\sigma'_0) - \ln \frac{(\sigma''_0 + \Delta\sigma)}{(\sigma'_0 + \Delta\sigma)} .$$

Since $|\sigma''_0 - \sigma'_0| \ll \sigma_0$, both $(\sigma''_0 + \Delta\sigma)/(\sigma'_0 + \Delta\sigma)$ and (σ''_0/σ'_0) are approximately equal to unity. One can write

$$\ln x \cong (x - 1) \quad \text{if } x \cong 1 ,$$

thus

$$\ln \frac{(1 + \Delta\sigma/\sigma'_0)}{(1 + \Delta\sigma/\sigma''_0)} \cong \left[\frac{\sigma''_0 - \sigma'_0}{\sigma'_0 + \Delta\sigma} \right] \frac{\Delta\sigma}{\sigma'_0} .$$

Substitute $\sigma''_0 - \sigma'_0 \cong \frac{d\sigma_0}{dT} \Delta T$, $\sigma'_0 = \sigma_0$ and $\sigma = \sigma_0 + \Delta\sigma$. Expression (21) then becomes

$$\frac{k}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \left[\ln(1 + \Delta\sigma/\sigma_0) - \frac{\Delta\sigma}{\sigma} \frac{T}{\sigma_0} \frac{d\sigma_0}{dT} \right] \Delta T .$$

Collecting terms the photo-thermoelectric emf can now be written (for $\Delta T \ll T$)

$$\Delta U = \frac{k}{e} \left\{ \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \left[\frac{N \mu_n \mu_p}{(\mu_n + \mu_p)(n_o \mu_n + p_o \mu_p)} \right] \left[\frac{\Delta \sigma}{\sigma} \right] + \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \right] \ln(1 + \Delta \sigma / \sigma_o) \right\} \Delta T$$

Define the photo-thermoelectric power by

$$\Delta \alpha = \lim_{\Delta T \rightarrow 0} \left\{ \frac{\Delta U}{\Delta T} \right\},$$

then making the substitution $b = \frac{\mu_n}{\mu_p}$ the photo-thermoelectric power is

$$\Delta \alpha = \frac{k}{e} \left\{ \left[\frac{b - 1}{b + 1} \right] \ln(1 + \Delta \sigma / \sigma_o) + \left[\frac{b}{b + 1} \right] \left[\frac{N}{bn_o + p_o} \right] \left[\frac{(\Delta \sigma / \sigma_o)}{(1 + \Delta \sigma / \sigma_o)} \right] \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \right\} \quad (22)$$

Equation (22) describes the photo-thermoelectric effect under the conditions where E_g can vary with temperature but the ratio of the mobilities b is assumed to be constant and independent of temperature. A more general expression was derived by Van der Pauw and Polder (1956) which contained an additional term with db/dT . However it was not deemed necessary to include the temperature dependence of b for this thesis since the experimental work was carried out in the temperature range between 300°K to 400°K , a region where changes in b are not expected to be great.

The original expressions by Tauc (1955a) were derived under the assumptions that both E_g and b were independent of temperature. However for work with CdS the value of $(1/k)(dE_g/dT)$ is of the same order of magnitude as Q_n/kT and Q_p/kT and it should therefore

not be left out.

Since Q_n and Q_p appear in equation (22), the significance of these quantities should be discussed in some detail. By definition $Q'_n = J_{nq} / J_{nN}$ and was called the mean value of the heat transported by an electron. Q'_n can be considered to be made up of two parts, an electronic part Q'_{ne} and a part which involves the electron interaction with the lattice. This latter component of Q'_n is only expected to be of significance at low temperatures and since all temperatures for this work were greater than 300°K any electron-lattice interaction component can be ignored. One simply writes

$$Q'_n = Q'_{ne} \quad \text{and} \quad Q'_p = Q'_{pe} \quad .$$

The electronic component can be determined from the equation for the current density of the electrons in a field ξ_x as given from the Boltzmann transport equation (see Dekker p. 282)

$$J_n = -eJ_{nN} = - \frac{2e^2 \xi_x}{3m_n^*} \int_0^\infty \tau_n \epsilon_n Z_n(\epsilon_n) \left(\partial f_{no} / \partial \epsilon_n \right) d\epsilon_n \quad .$$

Each electron participating in the current conveys an energy $E = E_g + \epsilon_n$, thus the heat current due to electrons is

$$J_{nq} = \frac{2e\xi_x}{3m_n^*} \int_0^\infty \tau_n \epsilon_n Z_n(\epsilon_n) (E_g + \epsilon_n) \left(\partial f_{no} / \partial \epsilon_n \right) d\epsilon_n \quad .$$

Hence

$$Q'_n = \frac{J_{nq}}{J_{nN}} = E_g + \frac{\int_0^\infty \tau_n \epsilon_n^2 Z_n(\epsilon_n) \left(\partial f_{no} / \partial \epsilon_n \right) d\epsilon_n}{\int_0^\infty \tau_n \epsilon_n Z_n(\epsilon_n) \left(\partial f_{no} / \partial \epsilon_n \right) d\epsilon_n} \quad .$$

Define $Q_n = Q'_n - E_g$ so that

$$Q_n = \frac{\int_0^\infty \tau_n \epsilon_n^2 Z_n(\epsilon_n) \left(\partial f_{no} / \partial \epsilon_n \right) d\epsilon_n}{\int_0^\infty \tau_n \epsilon_n Z_n(\epsilon_n) \left(\partial f_{no} / \partial \epsilon_n \right) d\epsilon_n} \quad .$$

Thus Q_n signifies the mean kinetic energy of transfer of the electrons.

If the relaxation time τ_n can be expressed as a power of the kinetic energy ϵ_n then the expression for Q_n can be solved for the case of classical statistics to give

$$Q_n = \left(\frac{5}{2} + r \right) kT \quad \text{where} \quad \tau_n \propto \epsilon_n^r.$$

Two limiting cases can be considered from simple theory.

(i) Scattering of current carriers by thermal lattice vibrations. In this case

$$\tau_n \propto \epsilon_n^{-\frac{1}{2}} \quad \text{which gives} \quad Q_n = 2kT.$$

(ii) Scattering of current carriers by ionized impurities. In this case

$$\tau_n \propto \epsilon_n^{\frac{3}{2}} \quad \text{which gives} \quad Q_n = 4kT.$$

For cases of mixed scattering Anselm and Klatchkin (1952) found that Q_{ne} lies within the limits of $2kT$ and $4kT$ for all the cases they studied. Their calculations were based on the assumption of spherical energy surfaces and apply for Q_{pe} as well.

Proposed application of the theory to the experimental study.

Germanium was studied in the work done by Tauc (1955) on the photo-thermoelectric effect. Since germanium is a poor photoconductor it was possible to make an assumption of weak illumination i.e. $\Delta\sigma/\sigma_0 \ll 1$. Using this assumption equation (22) gives the photo-thermoelectric power for germanium

$$\Delta\alpha = \frac{k}{e} \frac{\Delta\sigma}{\sigma_0} \left\{ \left[\frac{b-1}{b+1} \right] + \left[\frac{b}{b+1} \right] \left[\frac{N}{bn_0 + p_0} \right] \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \right\}.$$

If the germanium is n-type then $p_0 \ll n_0$ and $n_0 \cong N$ thus

$$\Delta\alpha = \frac{k}{e} \frac{\Delta\sigma}{\sigma_0} \left\{ \left[\frac{b-1}{b+1} \right] + \left[\frac{1}{b+1} \right] \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \right\}. \quad (23)$$

Then from experimental data if $\Delta\alpha$ is plotted against $\Delta\sigma/\sigma_0$ the slope of this straight line should yield $(Q_n + Q_p)/kT$ if b and dE_g/dT are known.

However in the work done for this manuscript on high resistance (i.e. $\sim 10^8$ ohm cm in darkness) cadmium sulfide, it is not justifiable to use the approximation of weak illumination, because CdS is strongly photoconducting. Even when the light intensity is relatively low $\Delta\sigma/\sigma_0$ can be much greater than unity. Furthermore weak illumination gives a very small ΔU which is extremely difficult to measure accurately in a high resistance source. The logical step then is to simplify equation (22) using the assumption that $\Delta\sigma/\sigma_0 \gg 1$. Then the photo-thermoelectric power is given

$$\Delta\alpha = \frac{k}{e} \left\{ \left[\frac{b-1}{b+1} \right] \ln(\sigma/\sigma_0) + \left[\frac{b}{b+1} \right] \left[\frac{N}{bn_0 + p_0} \right] \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \right\}$$

For the case of n-type semiconductors, $n_0 \gg p_0$ and $n_0 \cong N$

therefore

$$\Delta\alpha = \frac{k}{e} \left\{ \left[\frac{b-1}{b+1} \right] \ln(\sigma/\sigma_0) + \left[\frac{1}{b+1} \right] \left[\frac{Q_n + Q_p}{kT} - 3 - \frac{1}{k} \frac{dE_g}{dT} \right] \right\} \quad (24)$$

If the CdS sample is n-type, then a plot of experimental values of $\Delta\alpha$ verses $\ln(\sigma/\sigma_0)$ should yield a straight line, the slope of which will give a value for b and the intercept will give a value for $(Q_n + Q_p)/kT$.

That is

$$b = \frac{1 + (e/k)(\text{slope})}{1 - (e/k)(\text{slope})}$$

and

$$\frac{Q_n + Q_p}{kT} = \frac{e}{k} (b + 1)(\text{intercept}) + \frac{1}{k} \frac{dE_g}{dT} + 3$$

Frerichs (1947) in his work on CdS has shown that the absorption edge shifts linearly with temperature between 300°K and 700°K at a rate of -6.5×10^{-4} ev/°K. This figure can be related to the rate of change of the energy gap with temperature. Hence

$$\frac{1}{k} \frac{dE_g}{dT} = -7.5$$

and

$$\frac{Q_n + Q_p}{kT} = \frac{e}{k} (b + 1)(\text{intercept}) - 4.5$$

for cadmium sulfide.

It is noticed that information regarding only the sum $(Q_n + Q_p)/kT$ can be obtained by experimental study of the photo-thermoelectric effect. However the possibility exists that some useful information can be extracted from this quantity. According to the discussion given earlier Q_n and Q_p lie in the range $2kT$ to $4kT$. Hence if $(Q_n + Q_p)/kT = 8$ then one can assume that the scattering mechanism of the carriers is mainly due to ionized impurities. If $(Q_n + Q_p)/kT = 4$ then the scattering is mainly due to thermal lattice vibrations.

If b is large or the sample is intrinsic (ie. $N = 0$) then the photo-thermoelectric power will be given by

$$\Delta\alpha = \frac{k}{e} \frac{b-1}{b+1} \ln(\sigma/\sigma_0) \quad (25)$$

and the straight line resulting from a plot of $\Delta\alpha$ verses $\ln(\sigma/\sigma_0)$ will pass through the origin. A value for the mobility ratio can then be obtained from the slope of this line.

CHAPTER THREE

EXPERIMENTAL APPARATUS

Figure (3) gives a schematic diagram of the complete apparatus used for the experiment. The sample and sample holder were mounted inside an evacuated bell jar, the entire system being enclosed by an aluminum box to provide complete darkness for the sample. A source of light (500 watt high pressure xenon lamp) was positioned about five feet from the sample. The light was firstly focussed on a slit, the slit then focussed on the sample. This procedure illuminated only a narrow portion of the sample so that the contacts to the sample were in darkness at all times; see figure (4).

The specimen was held in the apparatus simply by pressure between two identical copper heat sinks. Figure (5) shows how two 10mm X 10mm X 1mm beryllium oxide plates were used to electrically insulate the sample from the heat sinks. Beryllium oxide was used because it provides a reasonably good thermal contact between the heat sinks and the sample as well as providing electrical resistance of better than 10^{13} ohms.

The heat sink on the right was mounted rigidly in teflon to prevent excessive heat loss. The left heat sink was also mounted in teflon, however it was moveable with a screw to apply the pressure to hold the sample in contact with the heat sinks. A winding of fibreglass coated constantan wire was placed on each heat sink to provide the necessary heating. This wire was capable of handling up to one ampere of current without overheating; the maximum power then dissipated was about twelve watts.

To minimize pickup one side of each heating coil and both heat sinks were electrically grounded. Also the aluminum box acted to shield the sample and electrical connections inside the vacuum. Ten electrical leads were taken from the evacuated area through a shielded vacuum-tight seal and were wired according to figure (6). Four

CROSS SECTION OF APPARATUS

FIGURE 3

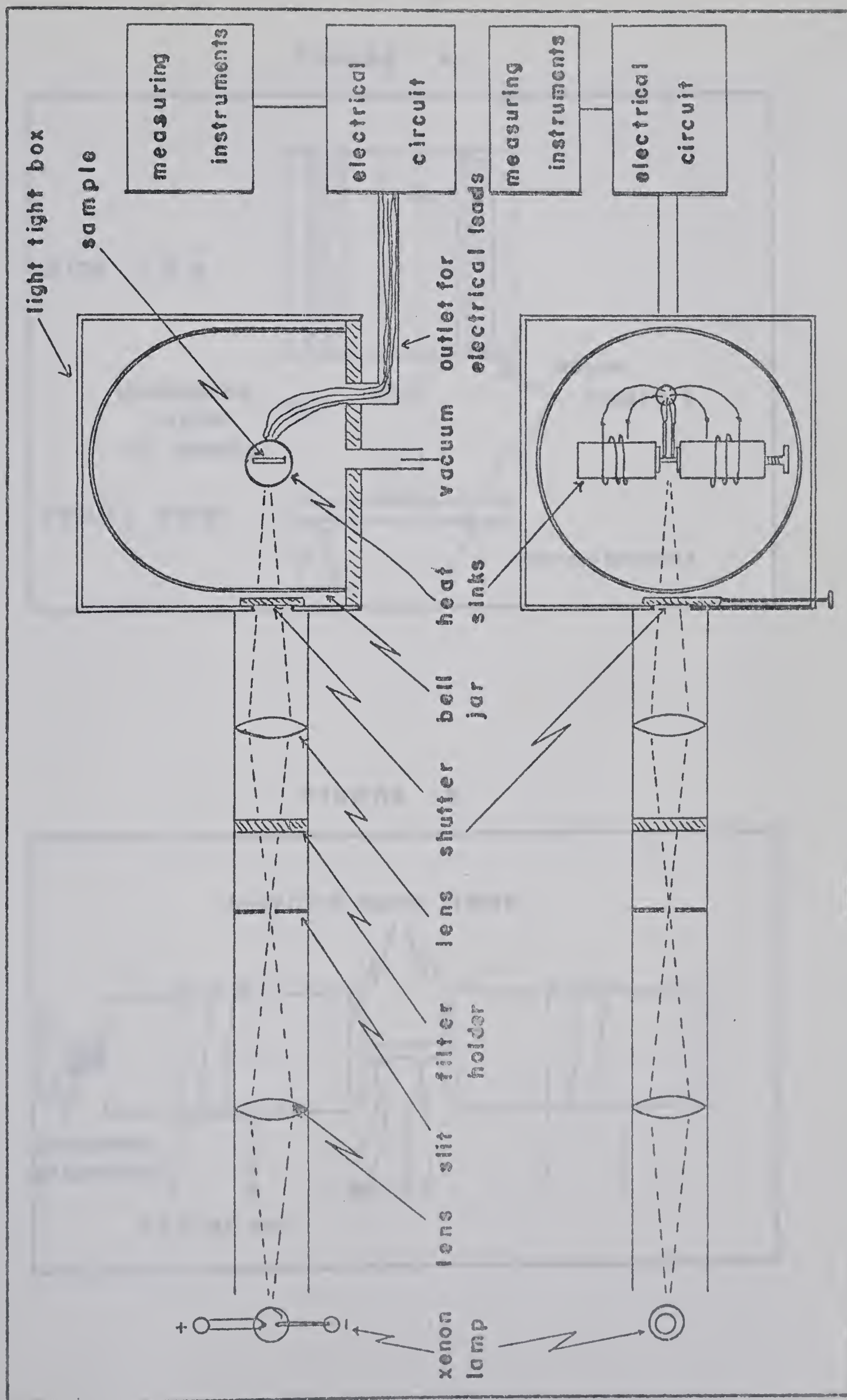


FIGURE 4

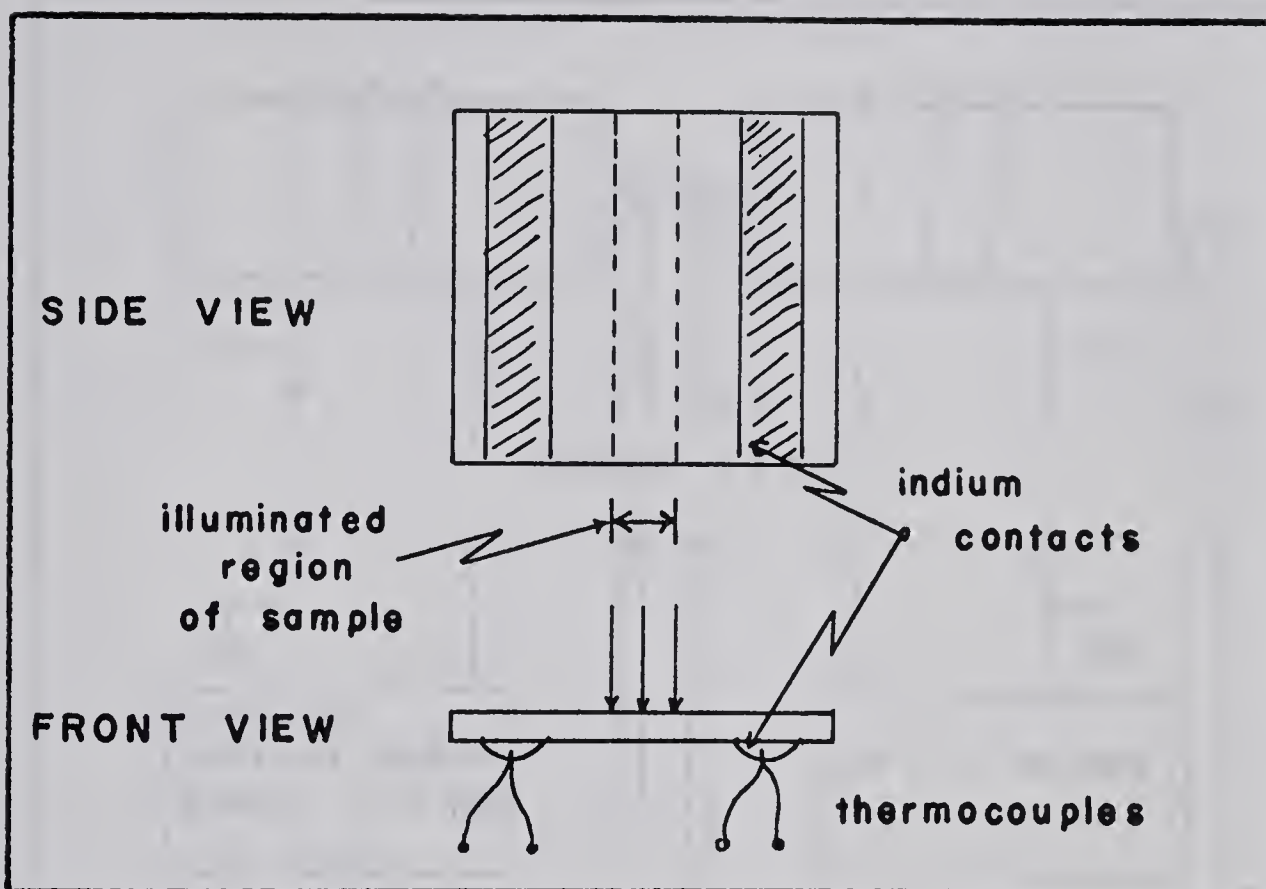


FIGURE 5

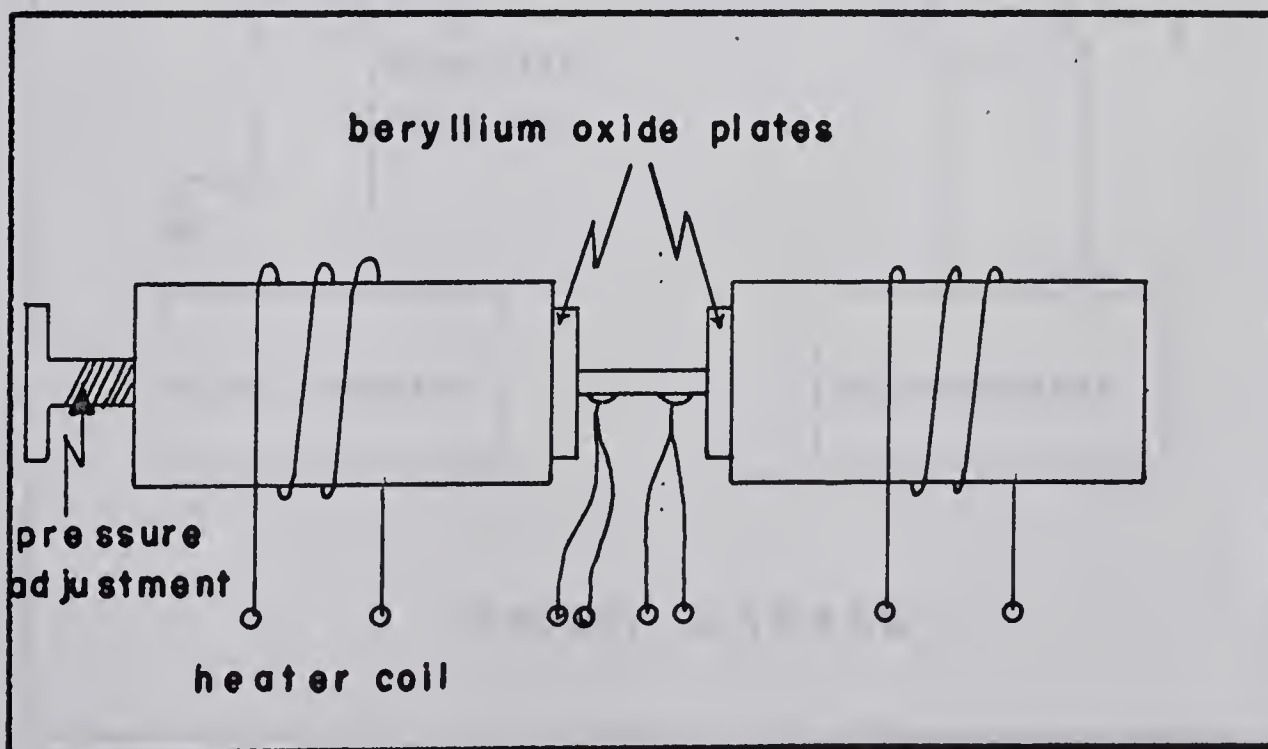
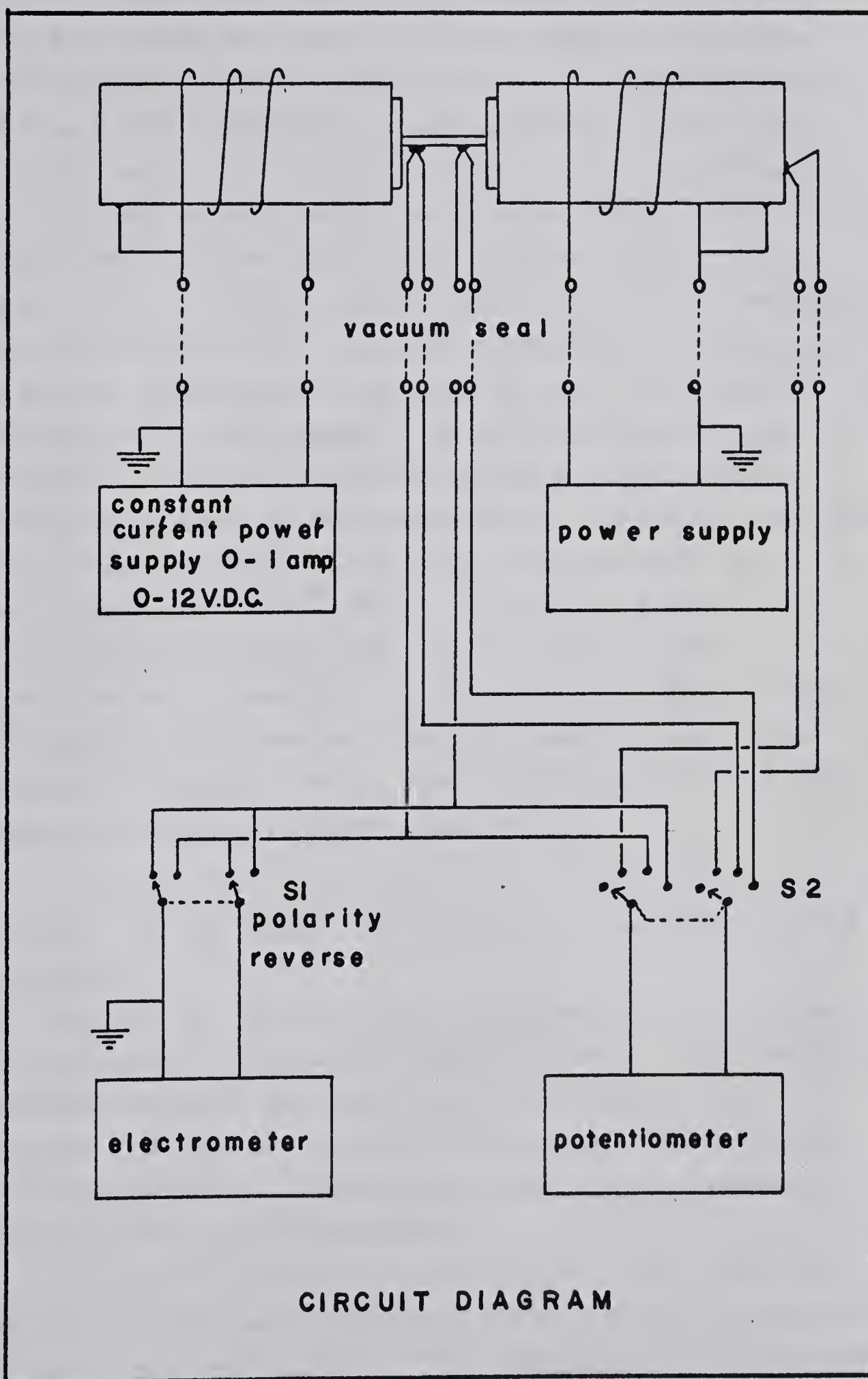


FIGURE 6



of these leads were for the current to the heaters, while the other six made up three copper constantan thermocouples, two of which went to the sample; the third was for temperature measurements of the right heat sink and had no significance to the experiment.

Voltage measurements were made between the copper leads of the two thermocouples touching the sample, with a General Radio Type 1230-A Electrometer. This electrometer has built-in circuitry for taking resistance measurements using a 9 volt D.C. source in series with the sample. This feature provided convenient conductivity measurements of the sample at various stages of the experiment. When the electrometer is being used for voltage measurements the input impedance is 10^{11} ohms. Since the sample resistance varied from 10^6 to 10^{11} ohms, some correction was necessary to the value of the voltage read on the electrometer when the sample resistance was near the upper limit. The true value of the emf across the sample is given simply by

$$U_{\text{actual}} = (U_{\text{elect.}}) (1 + R_s / 10^{11})$$

where R_s is the sample resistance at the time of the measurement.

Switch S2 allowed the electrometer to be used with all other instruments disconnected. When temperature measurements were desired, the electrometer was disconnected and S2 set for the proper thermocouple. The thermocouple voltages were read with a Leeds and Northrup Type B potentiometer.

It can be noticed in figures (4), (5), and (6) that the thermocouple contacts were placed on the sample away from the heat sinks. The reason for this procedure is that thermal resistance between sample and heat sink

is usually appreciable with semiconductors. Therefore it is necessary to use an arrangement analogous to the four-probe method for measuring electrical resistances. Thus the true temperature gradient in the sample must be measured by probes on the sample and not on the heat sinks.

CHAPTER FOUR

EXPERIMENTAL PROCEDURES

Commercially prepared samples of high-resistivity cadmium sulfide single crystals were obtained from Harshaw Chemical Company. These crystals were of dimensions 5mm X 5mm X 1mm and had no specified orientation. The following characteristics were supplied for the specimens by the company.

- 1) Absorption edge at 5200 Å with no major absorptions for wavelengths up to 15 microns.
- 2) Impurities detected spectrographically are less than one part per million of Al, Cu, Fe, Mg, Si, Li, Na, and Ca; about fifty parts per million of Zn; no other metal impurities detected.
- 3) Dielectric constant 11.6 .
- 4) Energy gap 2.4 ev.
- 5) Refractive index 2.43 .
- 6) Electron mobility $\mu_n = 295 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$.
- 7) Molecular weight 144.5 .
- 8) Density 4.8 gm cm⁻³ .
- 9) Melting point 1750 °C at 100 atmospheres.

Application of contacts to the CdS sample turned out to be a rather difficult problem. It was necessary to have two identical thermocouples make both thermal and electrical contact with the specimen. Copper constantan thermocouples were chosen for this job for two reasons; firstly they have a high thermoelectric power in the temperature range between 300°K and 400°K, and secondly the copper leads could be used as electrical contacts for the emf and for resistance measurements.

It is known that indium makes ohmic contact to cadmium sulfide, however it was found that the way in

which the contact was applied could greatly alter the properties of the contacts. Most publications on cadmium sulfide give little more than a passing remark to contact application. For example, typical reference might be "indium electrodes were evaporated on the crystal in high vacuum" (Van Vliet 1956).

Several attempts to apply thermocouple contacts to the sample were made with little success. One attempt was made to hold the thermocouples against an evaporated layer of indium by pressure. This procedure did make good thermal contact to the sample but unfortunately the electrical contact was not very ohmic. Another idea was tried whereby the thermocouples were held to evaporated indium on the sample by a silver paste. This method again gave poor electrical contacts.

It might be mentioned at this point that a very simple method for determining the type of contacts one has on photoconducting samples like CdS is outlined in a paper by Kanev et. al. (1965). This paper speaks of the "switch-off-effect" and the way in which this effect can determine the type of contacts on CdS single crystals. The method consists simply of measuring the photocurrent when a steady state is reached. The voltage V is turned off for a time t_{off} and then reconnected. If the photocurrent does not come back to its steady state value immediately the contacts are not perfectly ohmic.

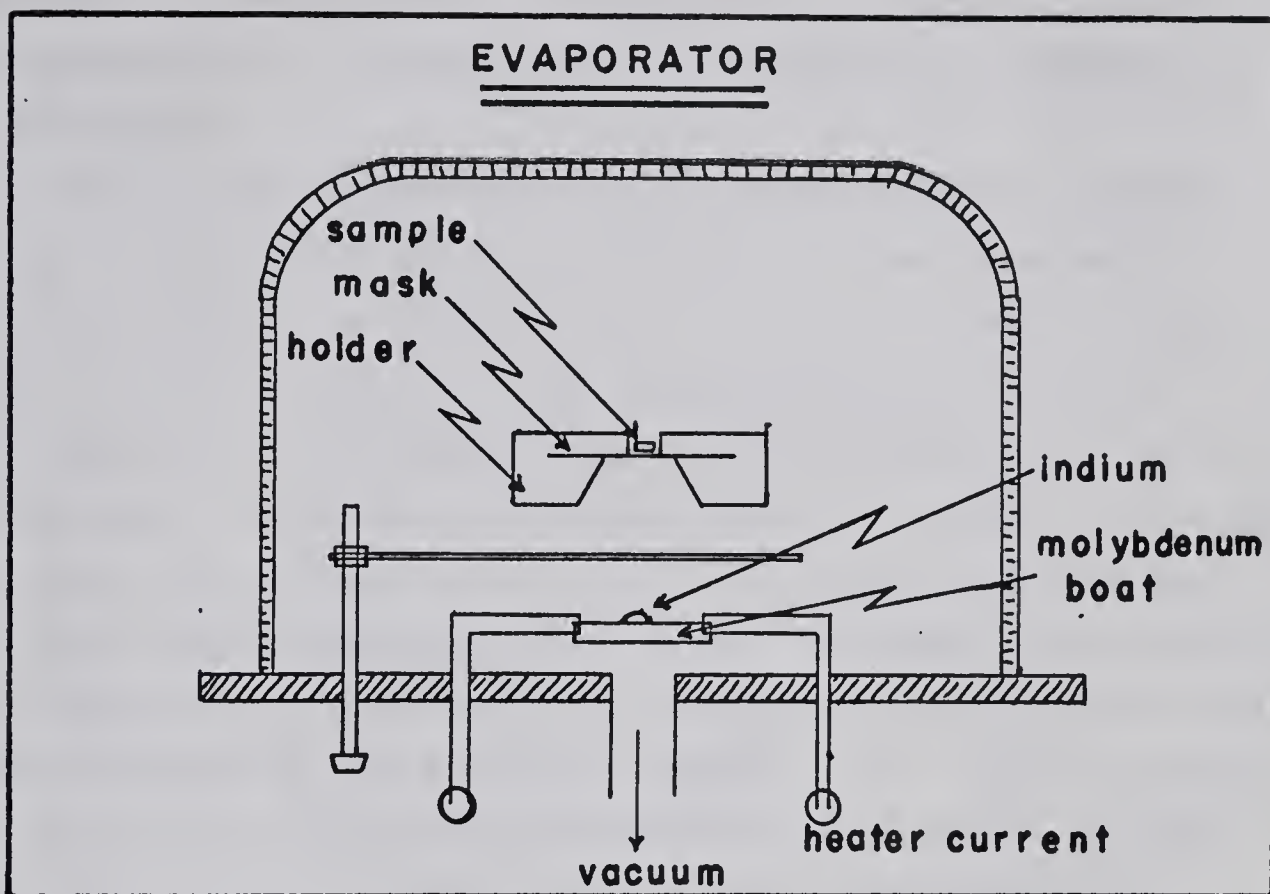
In the Journal of Scientific Instruments (vol. 42 p. 51, 1965) a detailed process for attaching electrical leads to bulk CdS crystals is given. A slight variation of this method was used with good success to apply copper constantan thermocouples on the specimen. Since good contacts are critical for good results, the complete method of contact application will be outlined.

In order to have good ohmic contacts two important points must receive special attention. Firstly the area of contact to the sample should be as large as possible. This measure is to insure that sharp changes of the current density in the region of the contacts will be minimized. Secondly the contact should not, if possible, be completely at the surface but instead the material making contact should be diffused into the volume of the sample. The purpose of the procedure is to minimize the possibility of sudden changes in the potential which may lead to a non-ohmic contact.

The method to be described is based on high vacuum evaporation (i.e. vacuum must be better than 10^{-6} torr) of indium on very clean crystals of CdS. Figure (7) shows a cross-section of the evaporator. The crystal was mounted in a holder containing a mask to expose only the desired portion of the sample to the indium (see figure 8). This holder was suspended about two inches directly above^a a molybdenum boat containing a small piece of clean indium. An additional moveable mask was used between the sample and the indium to expose the sample only for a desired length of time(about two minutes).

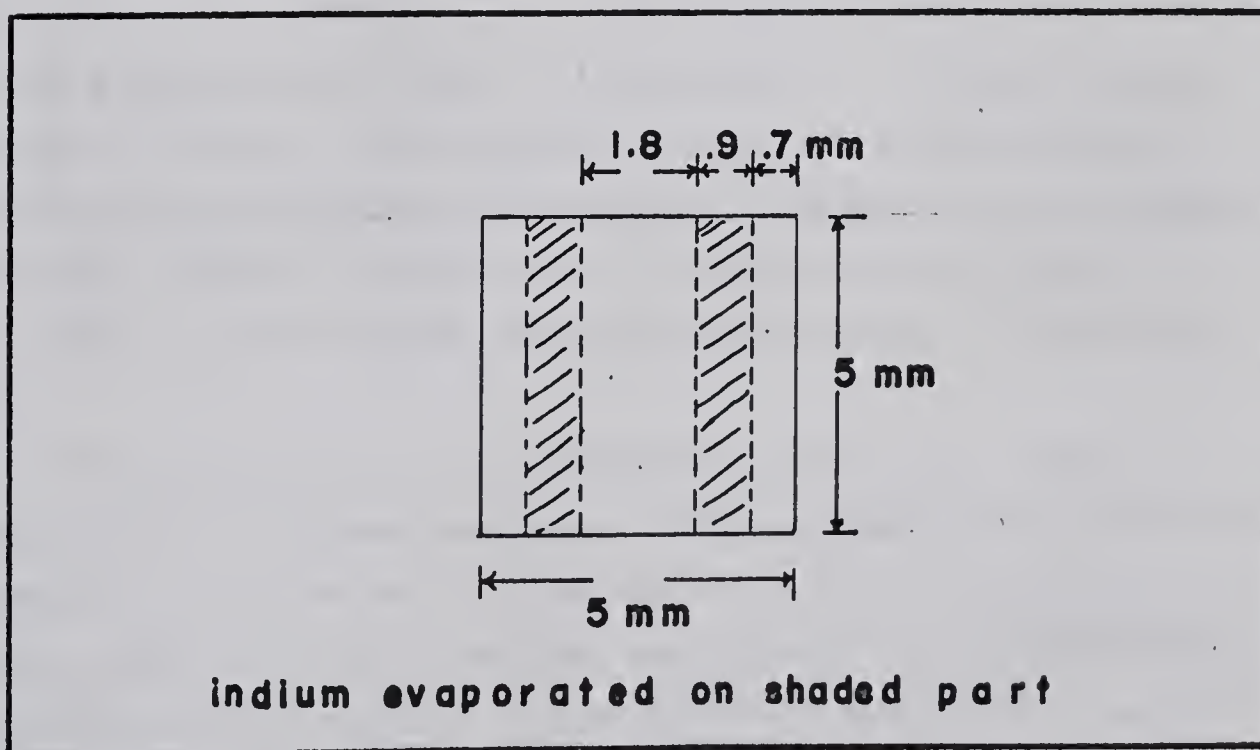
Before the sample was placed in the evaporator it had to be thoroughly cleaned in an etch of chromic acid. Chromic acid was prepared by dissolving 700 gms of chromic oxide in 2000 ml of distilled water and then adding 100 ml of concentrated sulfuric acid. The final etch solution consisted of the above diluted three times with distilled water and heated to 70°C . The sample was placed in this final solution for five minutes. Distilled water was then added continuously to the etch until the sample was eventually washed thoroughly, and it was then allowed to dry in air.

FIGURE 7



37

FIGURE 8



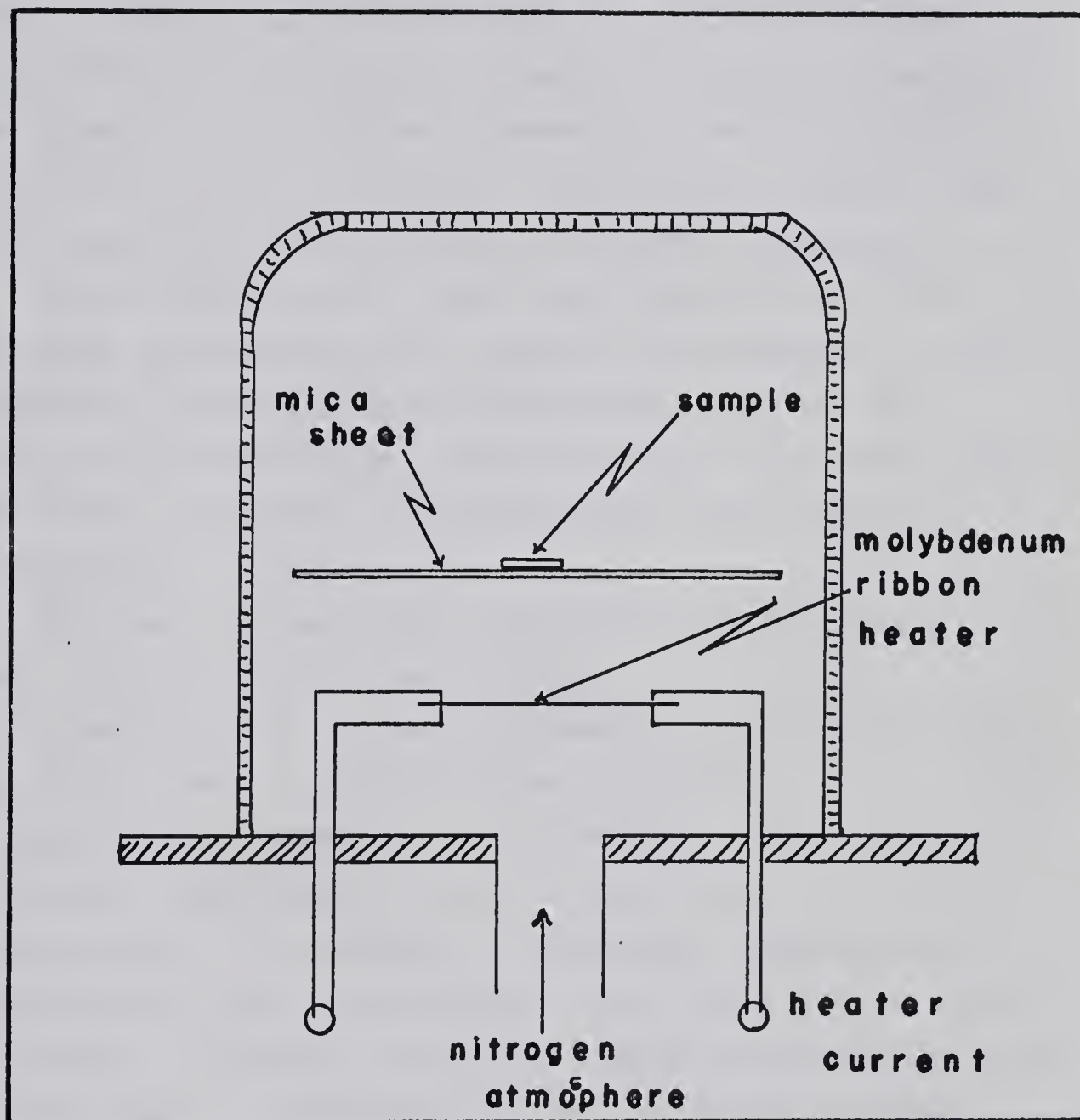
The indium used for the evaporation was also cleaned in a solution of chromic acid to remove any oxides on its surface.

After the evaporation was completed the sample had to be cooled completely before it was removed from the vacuum to insure that no oxide formed on the surface of the indium. The next step was to place the sample in a nitrogen atmosphere and heat it to a temperature above the melting point of indium (i.e. 154°C). This was done to allow some of the indium to diffuse into the sample or, in other words to 'wet' the surface. For this wetting process the evaporating equipment was altered slightly as shown in figure (9). After wetting the sample for about ten minutes it was again cooled completely before being removed from the nitrogen atmosphere.

Next freshly cut pieces of indium were pressed onto the evaporated film. These pieces were applied with a pressure that compressed the indium to about 80% of its original thickness. If the indium was completely free from oxide then the pieces would stick to the evaporated film on the sample. If the pieces failed to stick, the sample had to be recleaned in chromic acid and the evaporation and wetting processes repeated. Once the pieces of indium were firmly attached to the sample one could proceed to the next step.

Preparation of the thermocouples was done in a special way. Short pieces of #30 copper and constantan thermocouple wire were cleaned in a dilute solution of nitric acid and spot welded together. This ^{junction} was cleaned in nitric acid, washed thoroughly in distilled water and dipped in a molten solution of 50% lead and 50% tin.

FIGURE 9



WETTING APPARATUS

These 'tinned' thermocouple junctions were held against the indium blobs on the sample and the assembly was placed on a mica sheet in the wetting apparatus. The sample was next heated to a temperature above 154°C in a nitrogen atmosphere and the indium blobs fused to the tinned thermocouples creating a mechanically strong contact. Finally the sample was cooled completely and removed from the apparatus.

This complete unit was then mounted and the leads were soldered with a special low-thermal solder to identical thermocouple wires that made up the wiring of the apparatus. With the bell jar and light tight cover in place, the system was evacuated and the experiment started.

For each temperature gradient the following series of measurements were made.

- (1) The sample was allowed to remain in darkness for a sufficient length of time to allow non-equilibrium carriers to recombine. The voltage between the copper leads to the sample was then measured, followed by a resistance measurement.
- (2) The sample was illuminated with the type of light desired. Voltage and resistance measurements were made after a sufficient time had passed for a steady state to exist.
- (3) Temperature measurements were taken.

The voltages and resistances were measured as a function of the spectral distribution of the light using a set of interference filters to cover the spectrum very roughly from 4000 \AA to 8000 \AA . One filter was used at a time in step (2) and for each filter the cycle of steps (1), (2), and (3) was repeated. By proceeding in this way, any memory effects due to light of a different wave length should have been eliminated.

Every time the temperature was altered, twenty-four hours was allowed for a steady state to be established before measurements were taken. When measurements were being made with white light, the temperature was changed after every cycle (1), (2), and (3), hence only one set of readings could be made each day.

CHAPTER FIVE

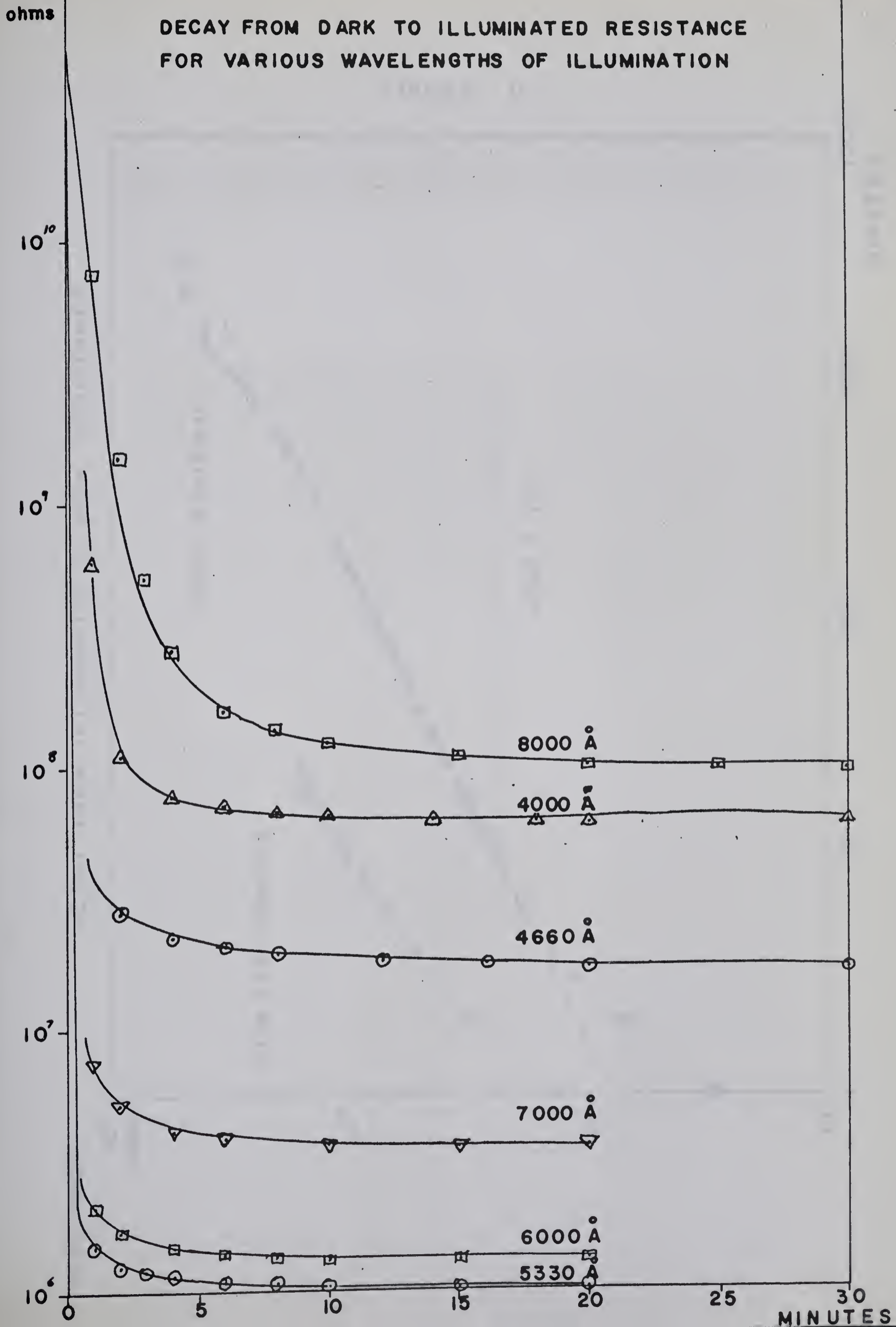
RESULTS

When the sample was illuminated a steady state condition could be reached only after a period of time had passed. Also when the illumination was discontinued a time was required for the properties of the sample to decay back to their equilibrium state in darkness. Initial measurements were taken of these transient effects to determine how long one had to wait before steady state measurements of the emf and resistance could be made. Figure (10) shows graphs of the resistance changes for several wavelengths of illumination started at time $t=0$. These curves were taken at room temperature and show that a steady state was usually not reached until at least twenty minutes had passed. Hence in step (2) of the procedure, measurements could not be taken until at least twenty minutes after the illumination was turned on.

Figure (11) shows the resistance decay back to the dark value and it is seen that this decay took an ^unusually long time. After 3000 minutes the resistance still appeared to be increasing, although very slowly. The scattering of the points near the high resistance end of the curve was probably due to changes in room temperature since there were long time intervals between these measurements. The portion of the curve for the times between 10 minutes and 400 minutes is of particular interest. The decay in this interval is almost perfectly linear on the log-log graph. The straight line drawn through these points has a slope of about 0.5 which shows that the resistance increased with time according to $t^{\frac{1}{2}}$,

FIGURE 10

RESISTANCE



DECAY FROM DARK TO ILLUMINATED RESISTANCE
FOR VARIOUS WAVELENGTHS OF ILLUMINATION

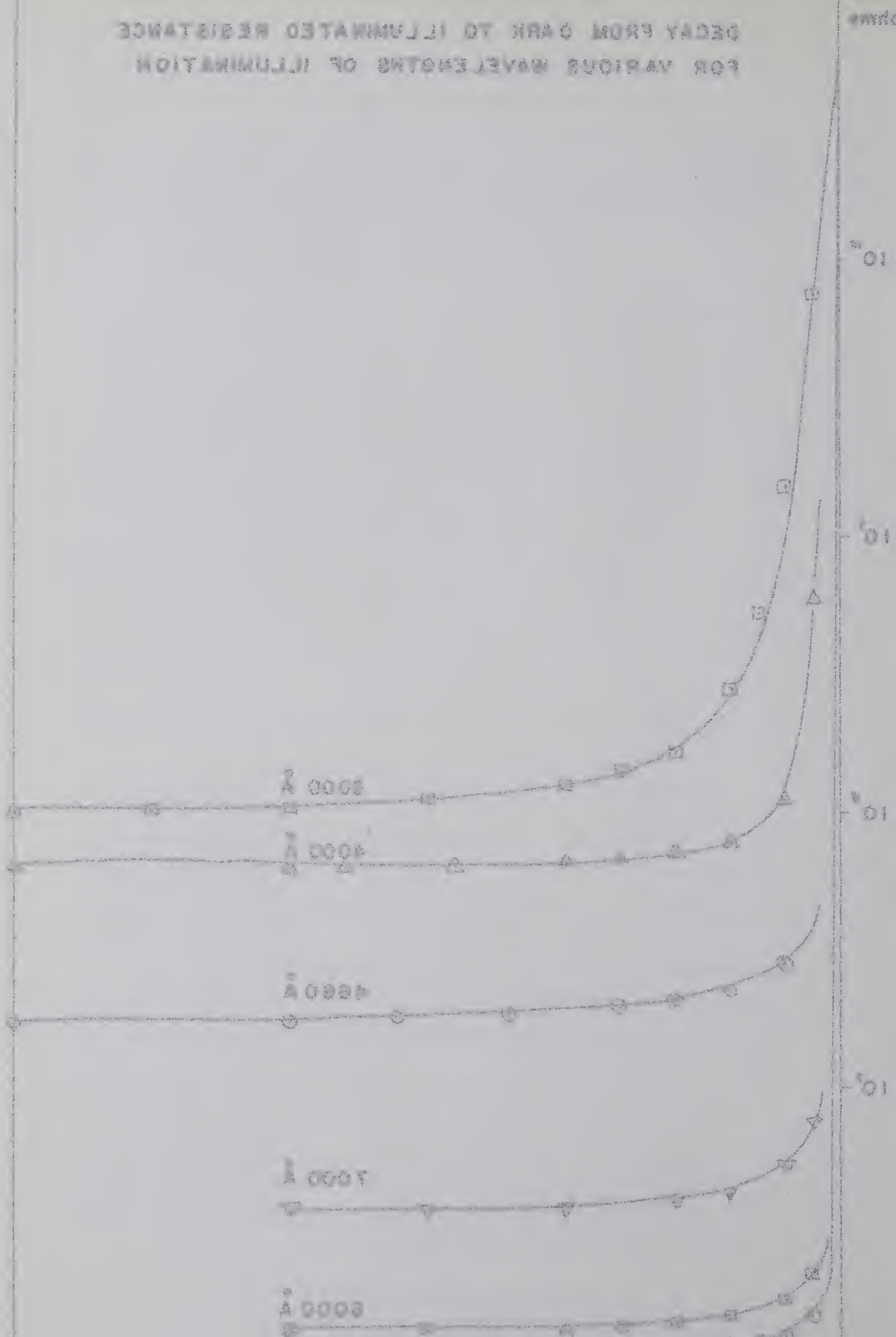
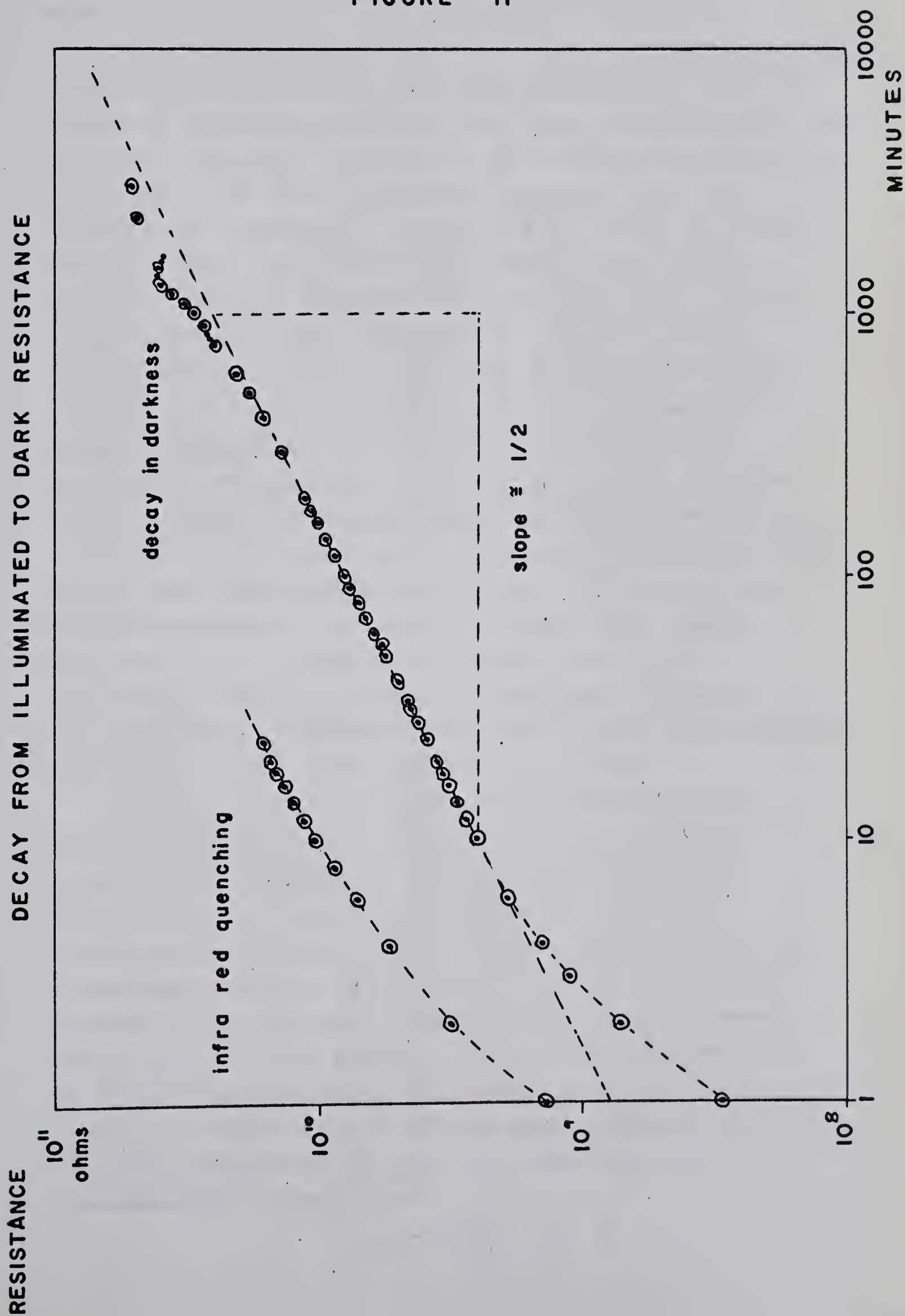


FIGURE II



or expressed alternatively the conductivity $\sigma \propto t^{-\frac{1}{2}}$ when (10 minutes $< t < 400$ minutes).

The decay back to the dark value of resistance could be greatly enhanced by "infra red quenching". That is to say by exposing the sample to light of wavelength 1.0μ the decay followed the second curve shown in figure (11). It is seen that the resistance increased from the illuminated resistance to about 2×10^{10} ohms in about thirty minutes with quenching, whereas for a free decay in complete darkness the time required to reach 2×10^{10} ohms was about 500 minutes. Because of this significant difference, infra red quenching was used in step (1) of the procedure to hasten the taking of measurements. However even with quenching about eight hours was usually allowed for step (1) in order to insure that dark equilibrium had been established.

The first measurements of the photo-thermoelectric effect were taken using white light. The results of these measurements are shown in table (1). Simple calculations were done on the quantities U_0 , U , R , R_0 and ΔT obtained from the experiment, to give the quantities of interest ΔU , $\alpha = U_0/\Delta T$, $\Delta\alpha = \Delta U/\Delta T$, and $\sigma/\sigma_0 = R_0/R$ which complete the table.

From the data of table (1) the thermoelectric power was plotted as a function of temperature in figure (12). Because of the scattered nature of these points it can only be concluded that the thermoelectric power did not change significantly with temperature between 40°C and 120°C , and thus it is assumed to be constant. Taking an average of these yields $\alpha_{av} = -1.14 \text{ mV/deg}$. Since the experimental value of α was negative, the sample must have been n-type or else the ratio of the mobilities was large. In either case equation (14) will describe the thermoelectric power, i.e.

$$\alpha = \frac{k}{e} \left\{ \frac{\xi_n}{kT} - \frac{Q_n}{kT} \right\}$$

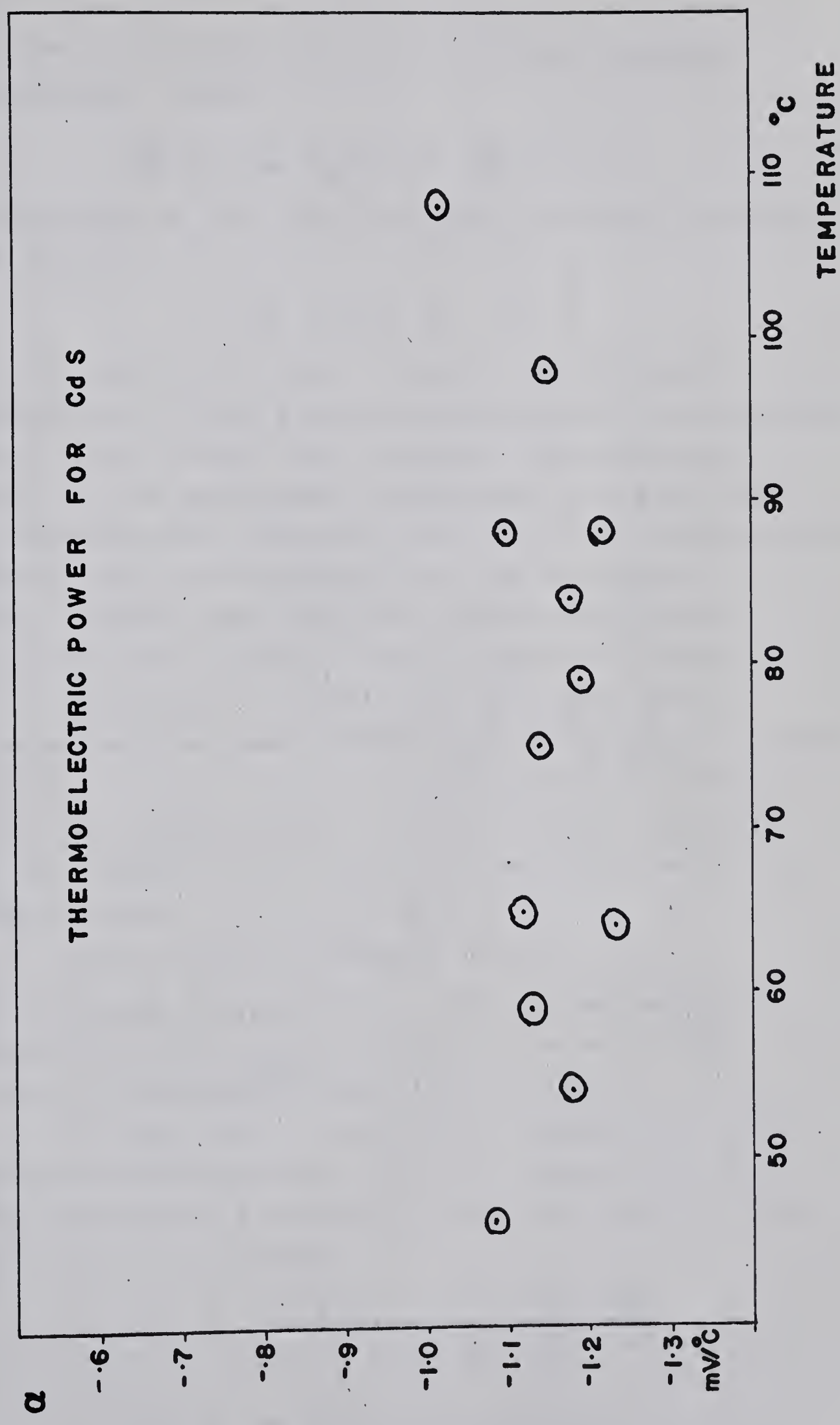
TABLE (1)

U_o mV	R_o $\times 10^6$ ohms	U mV	R $\times 10^6$ ohms	T $^{\circ}\text{C}$	ΔT $^{\circ}\text{C}$	α mV/ $^{\circ}\text{C}$	ΔU mV	$\Delta \alpha$ mV/ $^{\circ}\text{C}$	σ/σ_o	$\ln(\sigma/\sigma_o)$
- 6.6	34	-11.0	4.0	59	7.4	1.13	4.4	.59	850	6.8
- 7.1	15	- 9.5	4.0	75	7.4	1.14	2.4	.41	250	5.5
- 9.3	10.5	-12.3	8.7	84	7.85	1.18	3.0	.38	121	4.8
-15.8	7.3	-20.7	4.5	88	14.4	1.10	4.9	.34	162	5.1
-16.7	4.1	-21.0	15.0	98	14.5	1.15	4.3	.30	27.3	3.3
-16.9	2.3	-19.7	15.0	108	13.2	1.02	2.8	.21	15.0	2.7
- 7.4	23	-10.7	4.0	64	6.3	1.23	3.3	.52	575	6.4
-12.6	8	-15.9	13.7	79	9.83	1.19	3.3	.34	58.4	4.1
-13.7	5.3	-17.0	10.8	88	11.25	1.22	3.3	.29	49.0	3.9
- 4.3	48	- 6.3	11.6	46	3.96	1.08	2.0	.51	413	6.0
- 6.0	28	- 8.4	13.7	54	5.06	1.18	2.4	.47	204	5.3
- 8.5	15.3	-11.8	14.4	65	7.57	1.12	3.3	.44	106	4.7
- .26	160	- .55	1.8	28	.39	.67	.29	.74	8800	9.1

TABLE (2)

	n	y	x	x^2	xy
	1	.59	6.8	46.24	4.012
	2	.41	5.5	30.25	2.255
	3	.38	4.8	23.04	1.824
	4	.34	5.1	26.01	1.734
	5	.30	3.3	10.89	.990
	6	.21	2.7	7.29	.567
	7	.52	6.4	40.96	3.328
	8	.34	4.1	16.81	1.394
	9	.29	3.9	15.21	1.131
	10	.51	6.0	36.00	3.060
	11	.47	5.3	28.09	2.491
	12	.74	9.1	82.81	6.734
	13	.44	4.7	22.09	2.068
Σ		5.54	67.7	385.69	31.588

FIGURE 12



The value Q_n/kT should lie between the values 2, for lattice scattering and 4, for ionized impurity scattering. Hence

$$\frac{e\alpha}{k} + 2 \leq \zeta_n/kT \leq \frac{e\alpha}{k} + 4 .$$

Since $e\alpha/k \cong 13$ the following limits can be placed on ζ_n/kT ;

$$-11 \lesssim \zeta_n/kT \lesssim -13$$

in the temperature range between 40°C and 120°C . As a consequence of the above calculations the approximation used in the theory that classical statistics can be used, is now justified. Furthermore the fact that α is negative also indicates that the photo-thermoelectric effect will be described by one of equations (24) or (25), and that one need not consider the photo-thermoelectric equation for a p-type semiconductor.

The graph in figure (13) shows the photo-thermoelectric power plotted against $\ln(\sigma/\sigma_0)$. If the theory is correct this plot should yield a straight line with slope $(k/e)(b - 1)/(b + 1)$ and intercept at the origin for an intrinsic semiconductor or the intercept at

$$\Delta\alpha = \frac{1}{b + 1} \frac{k}{e} \left\{ \frac{Q_n + Q_p}{kT} + 4.5 \right\}$$

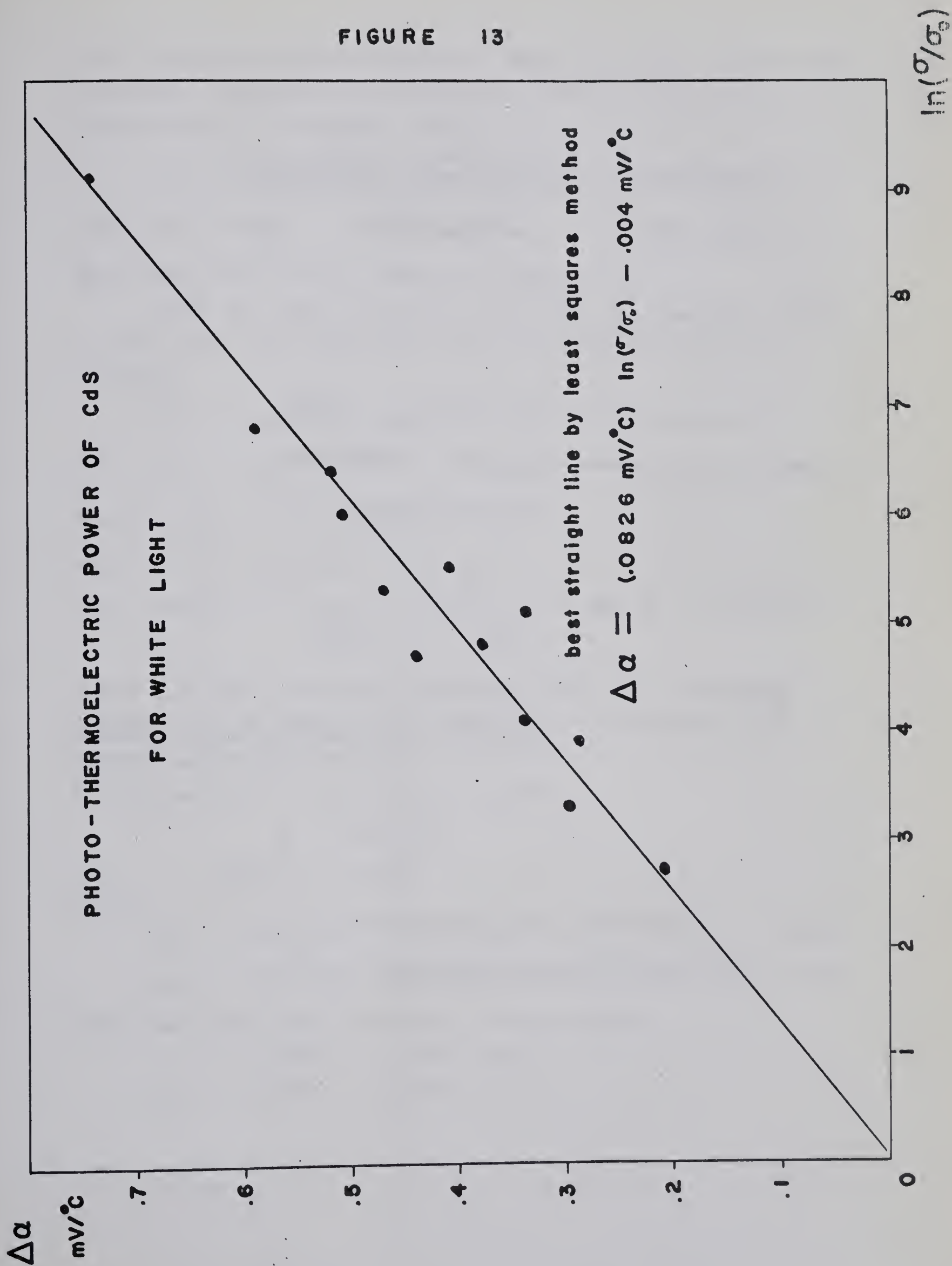
for a n-type semiconductor. The plotted points in figure (13) are quite scattered, however a trend toward a straight^{line} is definitely visible.

To find the best possible straight line to fit these points the method of "least squares" is used. This method for a straight line gives the best line as $y = Ax + B$, where

$$A = \frac{n(\sum x_i y_i) - (\sum y_i)(\sum x_i)}{n(\sum x_i^2) - (\sum x_i)^2}$$

$$B = (\sum y_i)/n - A (\sum x_i)/n$$

FIGURE 13



and n is the number of pairs of data (y_i, x_i) . Table (2) gives the values for the various sums needed for the calculation of A and B . Thus

$$A = \frac{13(31.588) - (5.54)(67.7)}{13(385.69) - (67.7)(67.7)} = .0826 \text{ mV/}^\circ\text{C}$$

$$\text{and } B = \frac{5.54}{13} - \frac{(.0826)(67.7)}{13} = -.004 \text{ mV/}^\circ\text{C}.$$

This best fit line is drawn on figure (11).

From the data given in table (2) the probable error in the slope and intercept can be determined from the formulas

$$P_A = r_e \sqrt{n/D} = \text{probable error in the slope } A,$$

$$\text{and } P_B = r_e \sqrt{\Sigma(x_i^2)/D} = \text{probable error in intercept } B.$$

$$\text{where } r_e = .6745 \sqrt{\Sigma(d_i^2)/(n-2)}$$

$$\text{and } D = n\Sigma(x_i^2) - (\Sigma x_i)^2$$

$$\begin{aligned} \text{and } \Sigma(d_i^2) &= \Sigma(y_i^2) - 2A\Sigma(y_i x_i) - 2B\Sigma y_i + A^2 \Sigma(x_i^2) \\ &\quad + 2AB\Sigma x_i + B^2 n. \end{aligned}$$

These formulas are taken directly out of the book The Mathematics of Physics and Chemistry by Margenau and Murphy pages 518 and 519.

A calculation of D and $\Sigma(d_i^2)$ gives

$$D = 430.68$$

$$\text{and } \Sigma(d_i^2) = .0155.$$

Hence

$$P_A = .6745 \sqrt{\{(13)(.0155)/(11)(430.68)\}} = .0044$$

$$P_B = .6745 \sqrt{\{(385.69)(.0155)/(11)(430.68)\}} = .024.$$

Thus the slope and intercept can be written

$$A = (.0826 \pm .0044) \text{ mV/}^\circ\text{C}$$

$$B = (-.004 \pm .024) \text{ mV/}^\circ\text{C}.$$

The slope of the best fit line gives a value for the mobility ratio of

$$b = \frac{1 + .0826/.0863}{1 - .0826/.0863} = 46 .$$

The mobility for the electrons at room temperature is about $295 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ according to the specifications supplied with the crystal. Therefore the hole mobility should be of the order $295/46 = 6 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$. From a direct measurement by Mort and Spear (1962) the hole mobility for CdS was reported to be between 10 and $20 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$. Thus the hole mobility found from the photo-thermoelectric effect is of the same order of magnitude. The probable error on the slope will mean that b could take on values as low as 20 and as high as infinity. The lower limit on b gives the hole mobility as $\sim 15 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$, thus this experiment has only been able to define the hole mobility between zero and $15 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$.

Furthermore, because of the large value for b and the uncertainty in B the intercept can tell virtually nothing about the sum $(Q_n + Q_p)/kT$.

Some measurements were taken using six interference filters to very roughly scan the frequency spectrum of visible light. The results of these measurements are listed in table (3). In figure (14) the conductivity of the CdS sample is plotted against wavelength for four different temperatures. It can be noticed from this graph that the peaks tend to shift to higher wavelengths as the temperature increases. A simple calculation will show that this shift is in agreement, at least to the order of magnitude, with the value used for dE_g/dT in the theory. That is, at $T = 25^\circ\text{C}$ the peak is approximately at 5500 \AA which is equivalent to an energy of 2.3 eV , and at $T = 120^\circ\text{C}$ the peak is approximately at 5700 \AA which is equivalent to an energy of 2.2 eV . Hence for a change in temperature of roughly 10^2 degrees the shift is -10^{-1} eV which gives $dE_g/dT \sim -10^{-3} \text{ eV/deg}$. This value is of the same order of magnitude as the value $-6.5 \times 10^{-4} \text{ eV/deg}$ used in the theory.

In figure (15) the photo-thermoelectric power is plotted as a function of wavelength. The curve for the lowest temperature has two peaks, the smaller peak occurring at a wavelength which is equivalent to the energy required to raise electrons across the energy gap. The other large peak is at 7000 \AA which is not sufficient energy for electrons to cross the forbidden band. Since the theory was developed under the assumption that all non-equilibrium carriers resulted from excitation across the forbidden band, it is not expected that this peak is explainable by the theory. In fact it is noticed that the conductivity curves do not show any maxima near 7000 \AA , so that the large values of the photo-thermoelectric power do not correspond to an increase in the conductivity as the theory predicts.

Table (3)

T °C	ΔT °C	U_o mV	α mV/°C	λ Å	U mV	R $\times 10^6$ ohms	ΔU mV	$\Delta \alpha$ mV/°C	$\sigma = 1/R$ $\times 10^{-10}$ ohms ⁻¹
63	11.4	-13.4	1.17	4000	-12.4	3100	-1.0	-.087	3.2
				4660	-16.8	95	+3.4	+.298	105
				5330	-16.1	2.9	+2.7	+.245	3300
				6000	-17.3	2.1	+3.9	+.342	4800
				7000	-19.1	30	+5.7	+.500	330
				8000	-13.5	2400	+ .1	+.009	4.2
80	15.6	-17.8	1.14	4000	-16.9	1600	- .9	-.058	6.2
				4660	-18.9	500	+1.1	+.071	20
				5330	-21.7	3.2	+3.9	+.250	3100
				6000	-23.6	2.1	+5.8	+.372	4800
				7000	-24.6	63	+6.8	+.436	160
				8000	-17.2	1400	- .6	-.038	7.1
120	12.6	-11.5	1.09	4000	-11.5	130	0.0	.000	77
				4660	-11.3	110	- .2	-.016	91
				5330	-12.1	80	+ .6	+.048	120
				6000	-12.3	58	+ .8	+.063	170
				7000	-11.2	96	- .3	-.024	100
				8000	-11.5	160	0.0	.000	62

FIGURE 14

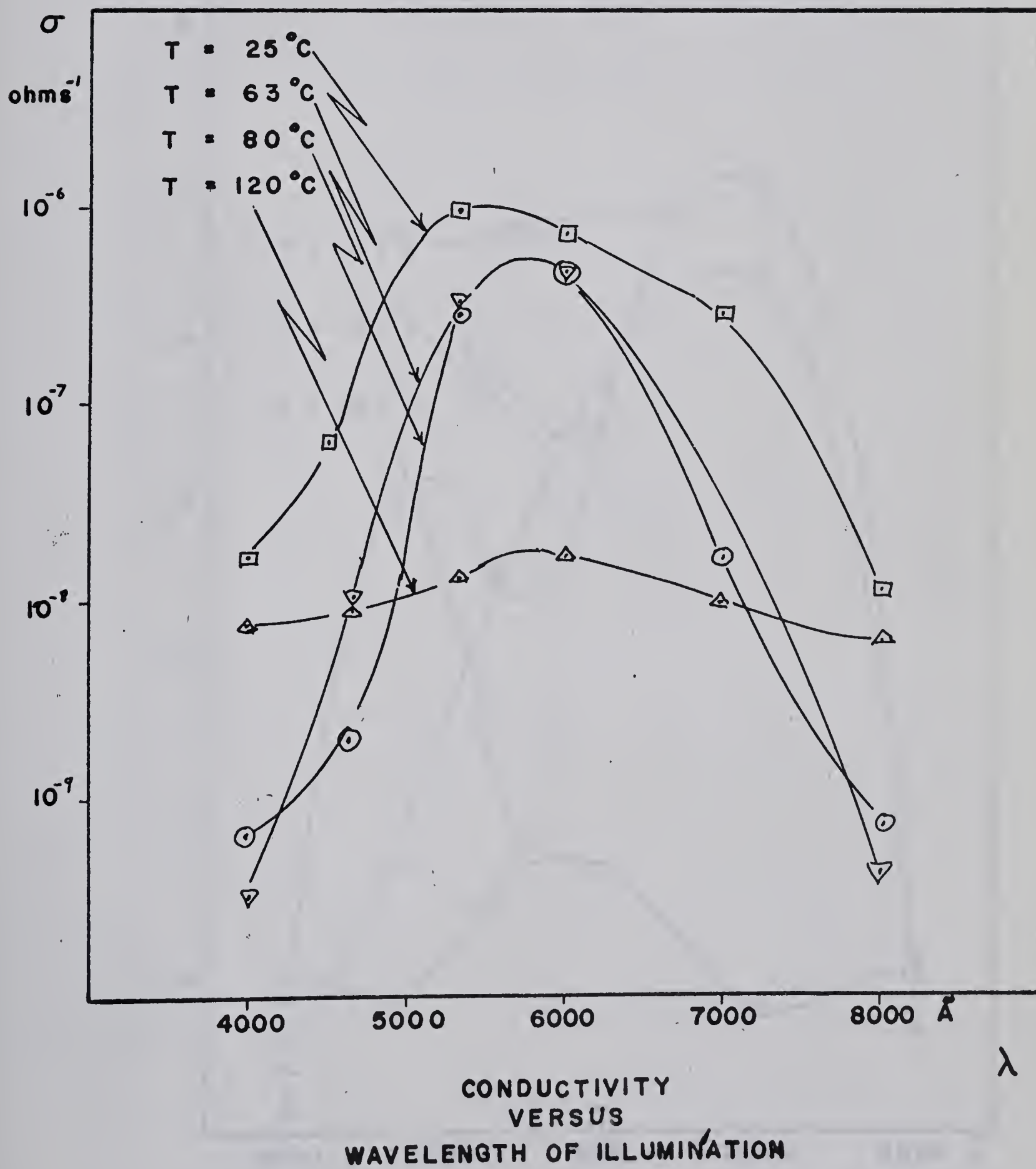
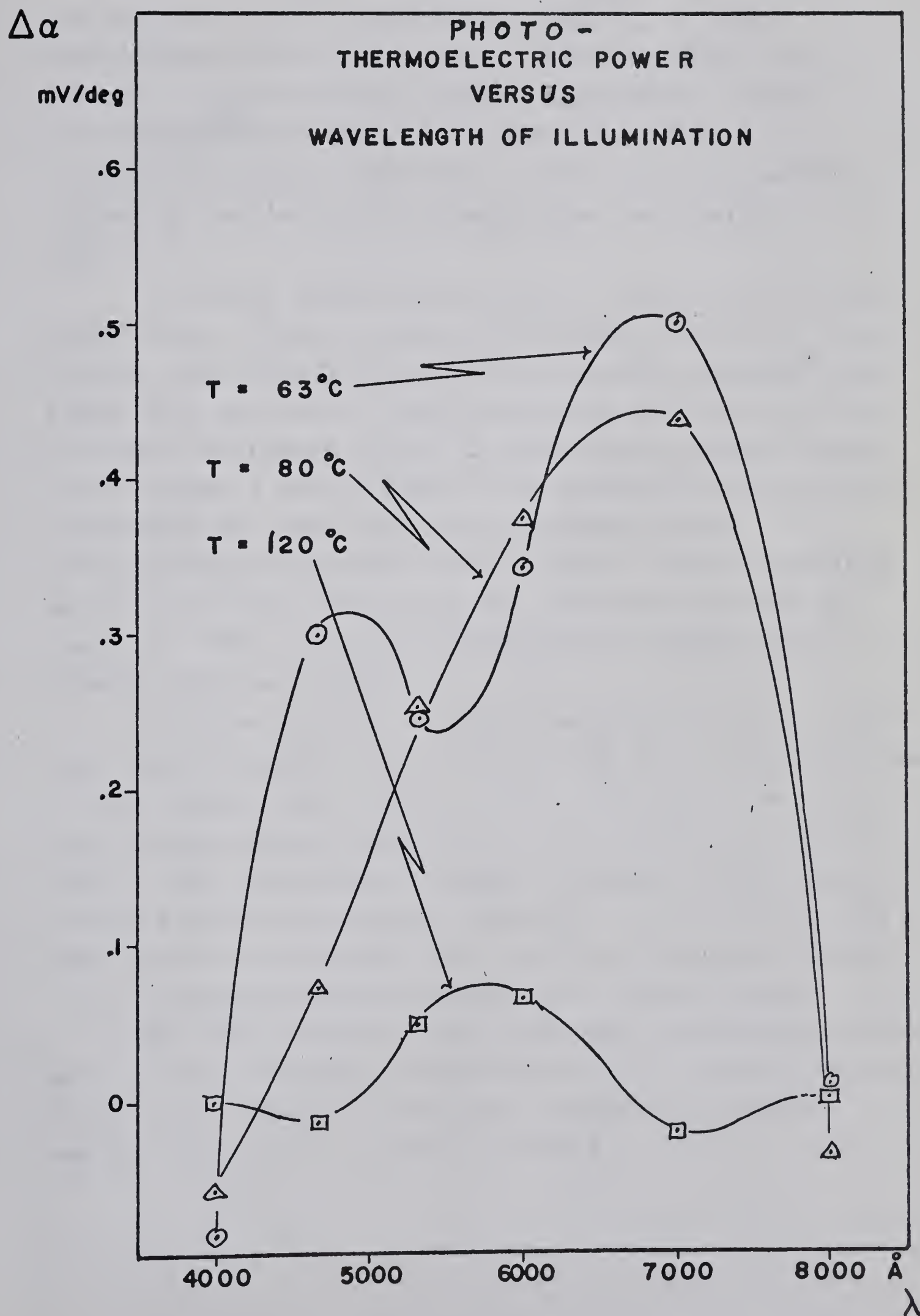


FIGURE 15



The curve for the temperature of 80°C only shows one maximum value, this being a 7000 \AA . A peak corresponding to the energy gap does not seem to be present. However since higher temperatures cause the energy^{gap} to decrease, the peak would be at a longer wavelength. Therefore a small peak is possibly hidden by the tail of the large peak centered at 7000 \AA .

At higher temperatures (e.g. $> 100^{\circ}\text{C}$) the thermal excitations become so great that light has little effect on the conductivity, therefore the photo-thermoelectric power will be small. This is noticed in the curve for $T = 120^{\circ}\text{C}$ in figure (15). In this curve however there is no longer a peak at 7000 \AA but instead the peak occurs at roughly the same place as the peak in the photoconductivity curve for $T = 120^{\circ}\text{C}$. It can possibly be concluded from this that the mechanism causing the peaks at 7000 \AA is less pronounced for temperatures greater than say 100°C .

Experiments done on CdS by Reynolds et. al. (1954a) also show a maximum value around 7000 \AA in their measurements of the photovoltaic effect. They noted that the size of this long/wavelength peak varied from crystal to crystal and in some cases was so large it mashed out the peak in the green light region. Reynolds (1954b) attributed this peak in the green light region as being the result of an intermediate band within the forbidden band.

The data observed here, although in relative agreement with related experiments done by others, is not complete or accurate enough to make any reliable conclusions on the basis for a maximum at 7000 \AA .

CHAPTER SIX

DISCUSSION

Examining the distribution of experimental points of the graph in figure (13), it is seen that errors in the experimental methods are quite large. It is constructive to consider some of the sources of these errors and possible ways they might be reduced.

The greatest single source of error lies in the measurement of ΔU . ΔU was measured by first measuring U_0 and then subtracting it from U . Thus the error in ΔU contains the errors in both U and U_0 . A logical method of reducing the error in ΔU is to try and measure it directly. This could be done by using pulsed illumination. Then Δu would approach a square wave which could be amplified and read directly, with D.C. components being ignored.

For CdS crystals a problem arises with this method because of the long decay times required to reach a steady state. If the light was to be pulsed too rapidly then only a small fraction of the total possible signal would appear in the pulsed output for ΔU . Furthermore the conductivity σ_0 in this ^{method} would not be the conductivity in absolute darkness but instead the conductivity for some mean illumination. Thus σ and σ_0 would not differ greatly and the approximation that $\sigma/\sigma_0 \gg 1$ might not hold. One therefore should consider using a light pulsed at ^a rate of about one cycle every thirty minutes. By following the traces over several cycles on a slow speed pen recorder the pulsed output signal ΔU could be read directly without regard to the values of U and U_0 . The values for the conductivities could be obtained at the end of the dark and light half cycles after a sufficient number of cycles

had passed so that a steady state had been reached. One might improve on this method by using infra-red illumination in the dark part of the cycle to hasten the approach to dark equilibrium.

More accuracy would be obtained if experimental values of $\Delta\alpha$ could be obtained for larger values of $\ln(\sigma/\sigma_0)$. There are two ways that this could be done. One way is to increase σ directly by using a more intense light source. This could probably be accomplished with the existing equipment by better use of lenses. It was noticed that the sample resistance in daylight was about 10^5 ohms. Since the lowest resistance obtained when the sample was in the equipment was about 10^6 ohms, there is at least room for an additional order of magnitude change in σ . The second method is to go to lower temperatures so that σ_0 is reduced considerably. The disadvantage to this latter idea is that U_0 is very hard to measure accurately when the resistance of the sample is extremely large.

Since the theory excluded all junction and contact effects, a source of deviation from the theory could result from light falling on the contacts. It was noticed when the apparatus was opened up that there was stray light falling on the contact areas of the sample. Therefore the experimental equipment might have been improved by using a mask directly in front of the sample to limit the illuminated portion to precisely between the contacts. Also the use of longer samples could have helped in this respect.

The theory used the assumption of linear geometry which meant that the concentration Δn should have been constant across the thickness of the sample. In other words for the experimental conditions to meet this assumption the sample thickness should have been less

than the reciprocal of the absorption coefficient. For illumination around 5000 \AA the absorption coefficient is about 10^2 cm^{-1} . Thus the sample should have been less than 10^{-2} cm thick. The sample used in the experiment was not this thin but instead was one millimeter in thickness. Therefore improvements might have been made if thinner samples were used.

CHAPTER SEVEN

CONCLUSIONS

The question is now raised as to whether the difficulty in achieving the improvements mentioned in the last chapter would be justified by the information that could be obtained. The theory shows that it should be possible to experimentally determine the mobility ratio and the sum of the mean kinetic energies of transfer for the electrons and holes. It is noticed from equations (23) and (24) that the mobility ratio can only be found independently of $(Q_n + Q_p)/kT$ for the case of strong illumination. That is to say for weak illumination the photo-thermoelectric power is proportional to $\Delta\sigma/\sigma_0$, the proportionality constant being dependent on both b and $(Q_n + Q_p)/kT$, but for strong illumination $\Delta\alpha$ is proportional to $\ln(\sigma/\sigma_0)$ and the constant is a function of b only.

Therefore with strongly photoconducting semiconductors the photo-thermoelectric effect could be used to measure b and $(Q_n + Q_p)/kT$. The draw back in this method occurs when b is large. For this case the slope of the plot of $(e/k)\Delta\alpha$ versus $\ln(\sigma/\sigma_0)$ approaches one. Since

$$b = \frac{1 + (\text{slope})}{1 - (\text{slope})}$$

a small uncertainty in the slope will mean a very large uncertainty in b . Therefore the accuracy must be very great. Hence the troubles that are necessary to obtain accuracy make this method undesirable. There are more direct methods of finding the mobilities that will give both the hole and electron mobilities even when b is large.

It might prove interesting to try measuring this effect in some materials that have mobility ratios close to one. In this case the slope of the line will approach

zero and the photo-thermoelectric power will be constant and independent of illumination if $\Delta\sigma/\sigma_0 \gg 1$.

Information about the sum $(Q_n + Q_p)/kT$ should be more easily obtained in this case.

Looking again at figure (15), the maximum value of the photo-thermoelectric power at 7000 Å suggests that spectral curves of the photo-thermoelectric effect may possibly be used to provide some information about impurity levels and other energy levels in the forbidden band.

By using a very large temperature gradient and chopped light, the output signal for ΔU would be large enough to be detected even for low intensities. Hence small changes in ΔU should show up easily when the wavelength of the incident light is changed to cover the spectrum. Possibly the fine structure of these curves of $\Delta\alpha$ versus λ could provide useful information. It might be worthwhile to look into this matter further.

BIBLIOGRAPHY

1. Clark and Woods, (1965) Journal of Scientific Instruments
volume 42, p. 51
2. Dekker,A.J. Solid State Physics, Prentice-Hall (1962)
3. Frerichs, (1947) Physical Review vol. 72 p. 594
4. Kanev et. al. (1965) Physica Status Solidi 9 K87
5. Kittel,C Introduction to Solid State Physics
John Wiley and Sons (1962)
6. Margenau and Murphy The Mathematics of Physics and
Chemistry D.Van Norstram 1957
7. Mort and Spear (1962) Physics Review Letters,vol.8, #8 p.314
8. Reynolds et. al. (1954a) Physical Review 96, 533
9. Reynolds et. al. (1954b) Physical Review 96, 1705
10. Tauc (1955a) Czechoslovak Journal of Physics 5, 528
11. Tauc (1955b) Czechoslovak Journal of Physics 5, 178
12. Tauc (1957) Reviews of Modern Physics 29, 308
13. Tauc,J Photo and Thermoelectric Effects in Semiconductors
Pergamon Press 1962
14. Van Vliet et. al. (1956) Physica 22, 723

B29837